



# ASSESSMENT OF SEDIMENT QUALITY IN DURBAN BAY - 2018



## **Report Details**

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### **Executive Summary**

Sediment accumulates naturally in ports. It may originate on land, from where it is transported by rivers and surface (stormwater) runoff into a port, and it may originate in the sea from where it is entrained into a port by tidal action. If the sediment is allowed to accumulate unchecked, a situation may be reached wherein the depth of navigation channels, turning basins, berths and other waters is reduced to the extent that safe vessel movement is not possible. As a result port authorities dredge navigation channels, berths and other facilities to their design dimension. In many ports and other navigable waterways this type of dredging is performed annually. The material in coastal ports is usually disposed offshore at designated unconfined disposal sites. In some countries, however, highly contaminated sediment is disposed in confined land or waterside facilities (e.g. capping). This is not a practice that has been followed to date in South Africa, where virtually all dredged sediment is disposed offshore (some sediment is used for shoreline nourishment or construction).

These include impacts on estuarine and marine organisms due to increased turbidity, destruction of communities of sediment-dwelling organisms, and toxic effects posed by contaminants remobilised from sediment. There are regulations that govern the act of maintenance dredging in South Africa, although the dredging party is expected to exercise a duty of care. The National Environmental Management Act: Integrated Coastal Management Act, 2008 (Act No. 24 of 2008) governs the openwater disposal of dredged material. Openwater disposal requires a permit. To comply with the Act, Transnet National Ports Authority annually makes an application to the Department of Environmental Affairs to dispose sediment maintenance dredged in Durban Bay at a registered openwater disposal site off Durban. The permitting procedure is in accordance with the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter of 1972 (the London Convention) and 1996 Protocol thereto, to which South Africa is a signatory. The Department decides if maintenance dredged sediment may be disposed at the openwater site based largely on metal concentrations in the sediment (other concerns and contaminants may come into play for dredging in certain ports, and for capital dredging). The Department may require biological testing of sediment if chemical analyses suggest a significant probability for toxic effects.

The need for a permitting procedure that considers contaminant concentrations in sediment identified for dredging and subsequent openwater disposal is that sediment is the major sink for many contaminants in aquatic ecosystems. There are a multitude of possible contaminant sources in ports, including the spillage of cargo, chemicals leached from antifouling coatings on vessel hulls, and vessel construction and maintenance. Contaminants are also introduced to ports from their usually urban and industrial surroundings. Surface (stormwater) runoff, for example, is an important source of many contaminants to ports. Ports are designed to provide a sheltered environment for the safe loading and offloading of cargo. This sheltered environment facilitates the deposition accumulation of mud and particulate organic matter, onto which many contaminants adsorb. Many contaminants are thus effectively retained in sediment in ports, and sediment in ports is thus invariably contaminated by a range of chemicals.

This report presents and discusses findings of the physical and chemical analysis and toxicity testing of sediment collected in Durban Bay in June 2018. The main purpose of this report is to provide Transnet National Ports Authority with some of the information required for the completion of a permit application to the Department of Environmental Affairs to cover openwater disposal of sediment maintenance dredged in Durban Bay for the next permit cycle. The report provides officials from the Department of Environmental Affairs with information for reaching an informed decision on the application.

Surficial sediment (upper 5 - 10 cm) for was collected at stations identified by Transnet National Ports Authority based largely on anticipated maintenance dredging requirements. In the laboratory the sediment was analysed for grain size, total organic content, and concentrations of

15 metals and 20 polycyclic aromatic hydrocarbon isomers.

From a textural perspective the sediment at most stations in Durban Bay in June 2018 is classified as muddy-sand or sandy-mud, but the sediment at several stations is classified as sand and at two stations as mud. The dominant grain size class at 20 of the stations was mud, at 11 stations was finegrained sand, and at ten stations was mediumgrained sand. The contribution of mud to the bulk weight of sediment varied widely, but as stated above at only two stations was it so high (≥90%) for the sediment to be classified as mud. All but two of the stations where mud was the dominant grain size class were situated in the upper part of the Bay. The findings for the 2018 survey are consistent with those of previous surveys. The high mud fraction of sediment in the upper part of Durban Bay reflects a combination of factors, including most importantly weak currents that characterise this part of the Bay and the input of mud-sized material via rivers that flow into the Silt Canal, which material largely settles from the water column in the upper part. All things being equal, the high mud fraction in the upper part of the Bay alludes to a greater propensity for the retention and accumulation of particle reactive contaminants than in the lower part. The propensity for contaminant retention is less in the lower part, due to the coarser-grained sediment in this part and its distance from the most significant sources of mudsized material to the Bay, namely rivers.

A baseline model was used to identify sediment that had a higher than expected total organic content. Superimposing the total organic content in sediment collected in Durban Bay in June 2018 onto the baseline model identifies the sediment at two stations in the Silt Canal, one station in Maydon Wharf Channel, and two stations in Esplanade Channel as enriched with particulate organic matter. Apart from the stations in the Silt Canal the enrichment was of a low magnitude. Particulate organic matter enrichment of sediment in the Silt Canal has been a more or less consistent feature of previous surveys. The excess particulate organic matter is almost certainly introduced by the Umbilo and Umhlatuzana Rivers. This said some of the particulate organic matter probably also has a

source in the port, including senescent microalgae that often reach bloom status in the Silt Canal due to the excessive introduction of nutrients by the rivers. The source of the excess particulate organic matter at stations in Maydon Wharf and Esplanade Channels is uncertain, but its introduction via the Canal Road culvert cannot be excluded considering the proximity of these stations to one another and the culvert. The findings for the 2018 survey are consistent with those of previous surveys from the perspective that sediment in Durban Bay has typically not been significantly enriched with particulate organic matter apart from in the Silt Canal, where the enrichment was often high.

Baseline models were used to identify sediment metals at a higher than concentration. The concentrations of most metals in sediment at most stations in Durban Bay in June 2018 fall within baseline model prediction limits, that is, they are within the expected baseline range for sediment in the Bay. The concentrations of one or more metals in the sediment at numerous stations did, however, exceed baseline model upper prediction limits, in some cases significantly. The sediment with the highest number of metals (ten) at an enriched concentration was at a station in the Silt Canal, off the inflow of the Umbilo/Umhlatuzana Rivers. Copper was the most frequently enriched metal, present at a higher than expected concentration in sediment at 23 of the 41 stations, followed by zinc at 18 stations, chromium at 16 stations, and nickel at seven stations. These have been the, or amongst the most frequently enriched metals in sediment in the Bay in previous surveys. The trend in metal contamination of sediment in Durban Bay in June 2018 is consistent with the findings of previous surveys.

Sediment at numerous stations in Durban Bay in June 2018 was contaminated by polycyclic aromatic hydrocarbons, four organochlorine pesticides, polychlorinated biphenyls and tributyltin. Polycyclic aromatic hydrocarbon, polychlorinated biphenyl and tributyltin concentrations were typically highest in sediment in the upper part of the Bay. Although butyltins were present in sediment at all stations, concentrations in the upper part of the Bay were generally considerably higher than in the lower part. There is a strong likelihood vessel

maintenance and construction facilities are an important source of polycyclic aromatic hydrocarbons and tributyltin, and possibly also polychlorinated biphenyls in sediment in Congella Basin. However, there is little doubt there are other anthropogenic sources of these chemicals to Durban Bay. The source of the pesticides is less certain, but probably also reflects inputs via rivers and surface runoff. High concentrations of some pesticides in Congella Basin might also reflect inputs from vessel maintenance and construction facilities.

The toxicological risk posed by chemicals in sediment was estimated using sediment quality guidelines. Metal concentrations were compared to the sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal. The copper concentration in sediment at 18 stations, zinc concentration in sediment at 11 stations, chromium concentration in sediment at two stations, and cadmium and lead concentration in sediment at single stations exceed the Warning Level. The copper, zinc and chromium concentration in sediment at eight, three and two of the stations also exceed Level I, and the copper and chromium concentration at Station 3 and chromium concentration at Station A the Level II. The copper concentration in sediment at Stations A and 2 and the zinc concentration in sediment at Station 3 is only slightly lower than the Level II. The greatest risks associated with the disposal of sediment in Durban Bay are thus for sediment in Congella Basin and nearby parts of Maydon Wharf Channel. Although sediment in the Silt Canal is also contaminated this part of the Bay is very rarely dredged.

The toxicological risk posed by organic chemicals in sediment in Durban Bay in June 2018 was estimated by comparing their concentrations to sediment quality guidelines used in North American coastal waters (known as Effects Range Low and Effects Range Median), to guidelines derived for freshwater ecosystems in North America (known as the Threshold Effects Concentration and the Probable Effects Concentration), or to guidelines derived by OSPAR )known as lower and upper

guidelines). The total polycyclic aromatic hydrocarbon concentration in sediment collected at a station at the Ship Repair Jetty in Congella Basin far exceeds the Effects Range Low, but is well the **Effects** Range Median. The below concentrations at other stations were generally well below the Effects Range Low. The Lindane concentration at two stations slightly exceeds the Threshold Effect Concentration, but is below the Probable Effects Concentration. The Dieldrin concentration at two stations also slightly exceeds the Threshold Effect Concentration, but is well below the Probable Effects Concentration. The DDX concentration in sediment at the ten stations where it was detected exceeds the Effects Range Low, but is well below the Effects Range Median apart from a station in the Silt Canal, where the concentration far exceeds the Effects Range Median. The tributyltin concentration in sediment at seven of the ten stations where analysed exceeds the lower guideline. The concentration at four of the stations also exceeds the upper guideline, considerably so in the case of two stations in Congella Basin and one station in the Point Basin

The fertilisation success of sea urchin gametes exposed to raw and 50% dilutions of elutriates prepared using sediment collected at four stations in Durban Bay in June 2018 showed that raw elutriates for two stations in the Silt Canal and one station in Congella Basin were toxic to the gametes. There was no toxicity evident when the elutriates were diluted by 50% with clean seawater. Raw and 50% diluted elutriates for sediment collected at a station at Little Lagoon presented no toxicity to sea urchin gametes. The elutriate test is designed to simulate water quality for up to about four hours after the openwater disposal of dredged sediment, or after contaminant release at a dredging site (either directly from sediment or in hopper overflow water if a trailer-suction hopper dredger is used). The implication of the elutriate toxicity testing is that the dredging of sediment at stations in Durban Bay for which testing was performed, and openwater disposal of dredged sediment could lead to the remobilisation/release of contaminants into the water column at concentrations that may pose an acute toxic risk to pelagic organisms. However, it is uncertain if this will only be restricted to organisms or their life stages that are similarly sensitive to toxicants as sea urchin gametes. One challenge with toxicity testing using sea urchin gametes is that they are highly sensitive toxicants, including ammonia and hydrogen sulphide that are commonly found at high concentrations in sediment porewater. However, these chemicals/compounds usually do not pose a risk to most marine animals in a dredging context as they are usually rapidly oxidised to less toxic forms after their release from sediment. It is not known how much ammonia or hydrogen sulphide was present in the sediment tested for toxicity in 2018.

Based on the comparison of metal and organic chemical concentrations in sediment collected in Durban Bay in June 2018 to sediment quality guidelines the greatest risk due to contaminant remobilisation during dredging will be in the Silt Canal, Congella Basin and part of Maydon Wharf Channel. There is also a potential risk of contaminant release when sediment dredged from these areas is disposed at the dredged material disposal site offshore of Durban. Contaminants in the sediment will be translocated to the dredged material disposal site, but it seems unlikely finegrained contaminated sediment will remain for long on the seabed due to the highly dispersive nature of this environment.

# **Table of Contents**

1.	Background and Report Purpose	Page 1
2.	Material and Methods	2
2.1.	General description of Durban Bay	2
2.2.	Fieldwork	3
2.3.	Laboratory analyses	3 3 3
2.3.1.	Accredited laboratories	3
2.3.2.	Grain size composition	3
2.3.3.	Total organic content	4
2.3.4.	Metals	4
2.3.5.	Organic chemicals and tributyltin	5
2.3.6.	Toxicity testing	5
3.	Results and Discussion	6
3.1.	Grain size composition	6
3.2.	Total organic content	7
3.3.	Metals	9
3.4.	Historical trends for metal concentrations	20
3.5	Organic chemicals and tributyltin	23
3.6.	Historical trends for organic chemicals and tributyltin	31
3.7.	Comparison of chemical concentrations to sediment quality guidelines	33
3.8.	Toxicity testing	39
4.	Conclusions	39
5.	References	41
6.	Appendices	44

#### 1. Background and Report Purpose

Sediment accumulates naturally in ports. It may originate on land, from where it is transported by rivers and surface (stormwater) runoff into a port, and it may originate in the sea from where it is entrained into a port by tidal action. If the sediment is allowed to accumulate unchecked, a situation may be reached wherein the depth of navigation channels, turning basins, berths and other waters is reduced to the extent that safe vessel movement is not possible. As a result port authorities dredge navigation channels, berths and other facilities to their design dimension. In many ports and other navigable waterways this type of dredging is performed annually. The material in coastal ports is usually disposed offshore at designated unconfined disposal sites. In some countries, however, highly contaminated sediment is disposed in confined land or waterside facilities (e.g. capping). This is not a practice that has been followed to date in South Africa, where virtually all dredged sediment is disposed offshore (some sediment is used for shoreline nourishment or construction).

Dredging poses numerous environmental impacts. These include impacts due to increased turbidity and suspended solids concentrations, destruction of communities of sediment-dwelling organisms in the dredging footprint, and toxic effects due to the remobilisation of contaminants from sediment. There are no regulations that govern the act of maintenance dredging in South Africa, although the dredging party is expected to exercise a duty of care. The National Environmental Management Act: Integrated Coastal Management Act, 2008 (Act No. 24 of 2008) governs the openwater disposal of dredged material. The openwater disposal of dredged material requires a permit from the Department of Environmental Affairs. To comply with the Act, Transnet National Ports Authority annually makes an application to the Department to dispose sediment maintenance dredged in Durban Bay at a registered openwater disposal site off Durban. The permitting procedure is in accordance with the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter of 1972 (the London Convention) and 1996 Protocol thereto, to which South Africa is a signatory. The Department decides if maintenance dredged sediment may be disposed at the openwater site based largely on metal concentrations in the sediment (other concerns and contaminants may come into play for dredging in certain ports, and for capital dredging). The Department may require biological testing of sediment if chemical analyses suggest a significant probability for toxic effects.

The need for a permitting procedure that considers chemical concentrations in sediment identified for dredging is that sediment is the major sink for many types of contaminants in aquatic ecosystems. There are a multitude of contaminant sources in ports, including the spillage of cargo, accidental and illegal discharge of oil from vessels, chemicals leached from antifouling coatings on vessel hulls, construction and maintenance vessel operations. Contaminants are also introduced to ports from their usually urban and industrial surroundings. Surface (stormwater) runoff, for example, is an important source of many contaminants to ports. Ports are designed to provide a sheltered environment for the safe loading and offloading of cargo. This sheltered environment facilitates the deposition accumulation of mud and particulate organic matter, onto which many contaminants adsorb. Many contaminants are thus effectively retained in sediment in ports, with the result that sediment in ports is almost invariably contaminated by a range of chemicals.

Dredging contaminated sediment is of ecological concern for two main reasons. First, the dredging process physically disturbs sediment, leading to changes in its characteristics (Eggleton and Thomas, 2004). For example, dredging results in the release of contaminants dissolved in sediment porewater (i.e. water between grains), while changes in the physical and chemical characteristics of sediment that occur during dredging may result in the remobilisation of contaminants adsorbed onto sediment grains and particulate organic matter. The influx of dissolved oxygen into sediment disturbed during dredging is particularly important as it results in an increase in sediment redox potential and a decrease in pH (mainly due to the oxidation of sulphides; Förstner, 1989). These changes alter particle-contaminant complexes, resulting in the

remobilisation of contaminants into the water column. Once remobilised, contaminants such as metals can remain in the dissolved (or free) form in the water column. This is the form in which metals are most bioavailable to organisms. This is important since contaminants can only exert a toxic effect if they are in a bioavailable form, that is, a form that can cross biological membranes. Some metals, such as iron and manganese, are rapidly precipitated after remobilisation through dredging disturbance and are deposited on sediment as insoluble oxides/hydroxides, to which other newly released metals adsorb at varying rates and extents (Di Toro et al. 1990; Caetano et al., 2002). As a result dissolved concentrations of metals usually peak near, but decrease sharply with distance from a dredging site as the metals are precipitated or otherwise scavenged from the water column (Goosens and Zwolsman, 1996).

There is little information available on the release of organic contaminants from sediment during dredging, and that which is available often provides conflicting information. For example, an increase in polychlorinated biphenyl concentrations has been detected a substantial distance from some dredging operations (e.g. USEPA 2009), while only minor increases in the immediate vicinity of dredging operations or no demonstrable increase have been reported in other cases (e.g. Bergen et al. 2005, Batelle 2007).

The second reason the dredging of contaminated sediment is of ecological concern is that contaminants are transferred to the dredged material disposal site if openwater disposal is permitted (e.g. Stronkhorst and van Hattum, 2003). As the dredged sediment descends through the water column to the seabed changes in its physical and chemical characteristics similar to those at a dredging site may release contaminants into the water column. Contaminants not released during descent to the seabed may be released over a protracted period as currents erode the sediment, gradually exposing contaminant laden sediment. Contaminants in the sediment may also adversely affect sediment-dwelling organisms at the disposal site by direct or indirect toxicity, limiting colonisation of the sediment and entering the food web. The propensity for sediment and associated contaminants to accumulate at a dredged material disposal site depends on whether it is in a dispersive or non-dispersive environment. Dispersive environments are characterised by strong currents that quickly erode fine-grained sediment and contaminants, limiting contaminant accumulation with time. The opposite is true for non-dispersive environments.

This report presents and discusses findings of the physical and chemical analysis and toxicity testing of sediment collected in Durban Bay in June 2018. The main purpose of this report is to provide Transnet National Ports Authority with some of the information required for the completion of a permit application to the Department of Environmental Affairs to cover openwater disposal of sediment maintenance dredged in Durban Bay for the next permit cycle. The report provides officials from the Department of Environmental Affairs with information for reaching an informed decision on the application.

#### 2. Material and Methods

#### 2.1. General description of Durban Bay

The Port of Durban is situated in Durban Bay, which is a large estuarine embayment in KwaZulu-Natal on the northeast coast of South Africa (29°52'S 31°02'E; Figure 1). It is South Africa's busiest port in terms of vessel calls and third busiest in terms of cargo volumes handled on an annual basis, and is amongst the busiest ports in Africa. The Bay has a total land and water surface area of about 1850 ha, of which the water surface area at high tide is about 890 ha. Most of the circumference of the Bay is armoured, with only a small part comprising soft shoreline. The entrance channel is dredged to a depth of about 17 m. The port has 58 berths, with draughts ranging between about 8 - 12 m. A large part of Congella Basin is set aside for vessel construction and maintenance. There are three areas that provide berthing for pleasure craft, namely the Point Yacht Club, Wilsons Wharf, and the extreme upper part of the Silt Canal.

The surroundings of Durban Bay are urbanised and industrialised. An estimated 57 stormwater outfalls direct surface runoff from the surroundings into the Bay, while three rivers (Umbilo, Umhlatuzana and

Amanzimnyama; Figure 1) flow into the so-called Silt Canal part of the Bay. The quality of water in the rivers is poor. This has resulted in water quality impairment in the Silt Canal, where the water column is typically characterised by high nutrient (nitrogen and phosphorous) and low dissolved oxygen concentrations. The sediment over a large part of Silt Canal is highly enriched with particulate organic matter and is anoxic (CSIR unpublished data).

Although port facilities have taken up much of Durban Bay, and the Bay has been extensively modified by the construction of these facilities, there remain extensive intertidal and shallow subtidal sandbanks and a remnant of the once extensive mangrove forest that characterised the Bay in the past (Figure 1). A large part of the remaining mangroves are protected in a Natural Heritage site. These sandbank and mangrove habitats serve an important ecological function, and lend aesthetic appeal. The Bay is as an important recreational venue for tourists and local communities, for activities that include fishing, sailing, canoeing and pleasure cruises.

#### 2.2. Fieldwork

Sediment was collected in June 2018 at 41 positions (stations) identified by Transnet National Ports Authority based largely on anticipated maintenance dredging requirements (Figure 1; see Appendix 1 for station Global Positioning System coordinates). The sediment at all stations was analysed for grain size, total organic content and the concentrations of 15 metals, while that collected at 12 - 15 of the stations was also analysed for polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls and/or butyltins. Elutriates prepared using sediment collected at four stations were tested for toxicity to sea urchin gametes.

The upper 5 - 10 cm (*i.e.* recently deposited) of sediment was collected using a small van Veen grab. On retrieval water overlying sediment in the grab was bled through a small hole in its side, taking care to lose as little fine-grained material as possible. The sediment was transferred to a glass bowl and inspected for the presence of anomalous material (*e.g.* plastic items). If the contents were comprised of a large amount of plastic items or

gravel, the contents were discarded and the grab was re-deployed. If the grab contents were deemed acceptable the sediment was homogenised in the glass bowl using a high-density polyethylene spatula. During this process shells, small stones, small plastic items and other material not deemed representative of the sediment were removed when encountered. Characteristics of the sediment, such as its colour, texture and aroma, were noted in field data sheets, and the sediment was then photographed. Aliquots of the homogenised sediment were then distributed between precleaned high-density polyethylene and amber glass jars. The samples were held on ice in the field and frozen (-18°C) on return to the laboratory. The grab was scrubbed with a hard brush, rinsed in site water, sprayed with hexane, and again rinsed in site water before the collection of sediment at a new station, to avoid cross contamination.

#### 2.3. Laboratory analyses

#### 2.3.1. Accredited laboratories

The bulk of the analyses on sediment were performed at environmental chemistry toxicology laboratories at CSIR campuses in Stellenbosch and Durban. The environmental chemistry laboratories are accredited by the South African National Accreditation System (SANAS) for the analysis of marine water, sediment and biological tissue samples. The laboratory SANAS accreditation certificates are provided in Appendix 2. Some analyses (e.g. polychlorinated biphenyls, butyltins) that no accredited laboratory in South Africa can perform at environmentally relevant detection limits were completed by the Australian Government National Measurement Institute, which is accredited by the National Association of Testing Authorities (NATA).

#### 2.3.2. Grain size composition

Sediment grain size composition was determined by wet and dry sieving the sediment into seven grain size classes according to the Wentworth Scale, namely mud (<0.063 mm), very fine-grained sand (0.063 - 0.125 mm), fine-grained sand (0.125 - 0.250 mm), medium-grained sand (0.25 - 0.50 mm), coarse-grained sand (0.5 - 1.0 mm), very coarse-grained sand (1.0 - 2.0 mm) and gravel (>2.0 mm).



Figure 1. Aerial view of Durban Bay, showing place names mentioned in the text.



**Figure 2.** Aerial view of Durban Bay, showing the positions (stations) where sediment was collected for physical and chemical analysis and toxicity testing in June 2018. Sediment collected at each station was analysed for grain size, total organic content and metals, while that collected at stations denoted in pink was also analysed for polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls and/or butyltins. Elutriates prepared from sediment collected at stations denoted in pink-orange was also tested for toxicity to sea urchin gametes.

#### 2.3.3. Total organic content

An aliquot of sediment was oven dried, weighed, and organic matter then degraded using hydrogen peroxide. The sediment was rinsed in distilled water, dried and weighed. The difference in dry

weight before and after organic matter degradation was used to determine the total organic content.

#### 2.3.4. Metals

The sediment was freeze dried and ball-milled.

About 1 g of dried sediment was weighed into a digestion vessel and digested in a mixture of HNO<sub>3</sub>-HCl-H<sub>2</sub>O<sub>2</sub> according to USEPA method 3050B. This is a 'near-total' digestion method that dissolves most elements that could become 'environmentally available', but is not designed to dissolve metals tightly incorporated in silicate structures. The digestate was filtered (0.45  $\mu$ m), diluted to volume with Milli-Q water, and the concentrations of various major, minor and trace metals detected and quantified using Inductively Coupled Plasma Optical Emission (ICP-OES) and Mass Spectroscopy (ICP-MS). Mercury was analysed using a direct mercury analyser (DMA).

Procedural blanks were analysed to assess laboratory contamination. Precision and extraction efficiency of the digestion and metal determination procedures was evaluated by analysing marine sediment reference standard PACS-2 (National Research Council of Canada). Since the reference material is certified for total digestion the recovery of several refractory metals (e.g. aluminium, chromium) was, as expected, somewhat below 100% (Table 1). However, all extractions were within acceptable tolerance and precision limits defined by the CSIR for quality assurance and quality control purposes.

Although arsenic is technically a metalloid (*i.e.* semi-metal), in the interests of simplicity it is referred to as a metal in this report.

#### 2.3.5. Organic chemicals and tributyltin

A suite of polycyclic aromatic hydrocarbon isomers, organochlorine pesticides and/or their metabolites,

polychlorinated biphenyl congeners, and mono-, diand tributyltin were analysed in sediment collected at 12 - 15 of the stations (Figure 1). The sediment was first freeze dried and ball-milled. Targeted chemicals were then extracted from weighed aliquots of the dried sediment using procedures based on those defined by the United States Environmental Protection Authority, or by the Australian Government National Measurement Institute. The extracts were subjected to a clean-up procedure to remove interfering substances and concentrated. The targeted chemicals were identified using a Gas Chromatograph-Mass Spectrometer, Gas Chromatograph with Electron Capture Detector, and Gas Chromatograph-Inductively Coupled Plasma Mass Spectrometer. Quantification was relative to internal and external standards.

Procedural blanks, matrix spikes and sample replicates were analysed with sample batches to assess laboratory contamination and analytical accuracy and precision. All chemicals were at concentrations below the method detection limit in procedural blanks. With few exceptions surrogate recoveries from spiked blanks and matrix spikes fell within data quality objectives.

#### 2.3.6. Toxicity testing

The toxicity of elutriates prepared using sediment collected at Stations A and C in the Silt Canal, Station F in Congella Basin, and Station G at Little Lagoon (Figure 1) was tested in the laboratory using the sea urchin fertilisation test. Elutriates were prepared by mixing one part sediment and three parts seawater (on a volume to volume basis,

Table 1. Recovery (%) of metals from standard reference material PACS-2 (National Research Council of Canada).

Replicate	Al	Fe	As	Ве	Cd	Cu	Cr	Mn	Hg	Ni	Pb	V	Zn
1	47.3	72.7	77.6	95.3	92.6	101.7	78.7	66.9	102.2	88.5	87.2	79.0	100.3
2	47.0	72.5	74.6	95.3	91.0	100.8	78.7	66.2	97.5	88.7	88.3	78.2	100.6
3	44.6	73.9	72.9	96.7	94.5	104.6	78.2	67.6	97.8	86.4	85.1	79.1	95.7
4	44.0	73.4	74.3	89.6	88.2	104.9	76.9	66.9	100.1	90.0	86.2	78.3	96.0
5	43.7	70.8	77.6	94.8	92.3	101.9	77.2	65.6	100.1	86.2	87.8	78.3	97.3
6	44.2	69.6	78.2	89.1	94.2	102.9	78.7	66.3	95.0	87.7	88.3	77.3	97.5
7	46.6	72.7	76.6	94.2	90.8	107.4	74.0	66.9	102.2	86.0	87.2	79.0	98.2
8	47.0	72.5	77.6	97.0	91.2	108.1	72.7	66.2	97.8	86.5	88.3	78.2	97.8
Mean	45.6	72.3	76.2	94.0	91.8	104.0	76.9	66.6	99.1	87.5	87.3	78.4	97.9
Standard deviation	1.6	1.4	2.0	3.0	2.0	2.7	2.3	0.6	2.5	1.5	1.2	0.6	1.8
Minimum	43.7	69.6	72.9	89.1	88.2	100.8	72.7	65.6	95.0	86.0	85.1	77.3	95.7
Maximum	47.3	73.9	78.2	97.0	94.5	108.1	78.7	67.6	102.2	90.0	88.3	79.1	100.6
Variance	2.4	2.0	3.8	9.0	4.1	7.2	5.3	0.4	6.3	2.1	1.3	0.4	3.2

seawater collected at Vetch's Beach in Durban) in glass containers. The contents of the containers were then placed on a shaker and agitated at 1000 rpm for one hour. The contents were allowed to settle. Although the targeted settling time was four hours, for some samples there was still a significant amount of fine-grained material in suspension after this period. The contents were thus centrifuged. The raw elutriate and a 50% dilution of the elutriate were tested.

Adult sea urchins (*Tripneustes gratilla*) were collected at Vetch's Beach and maintained at ambient temperature in natural seawater in large, flow-through tanks in the laboratory. Gametes were obtained by inducing sea urchins to spawn, by injecting 1 - 2 ml of 0.5 molar potassium chloride (KCl) solution into the coelomic cavity of each test organism. Gametes from males and females were collected separately. Females were inverted over glass beakers filled with seawater and eggs were allowed to settle. Sperm was collected 'dry' in pasteur pipettes. Sea urchins that provided relatively little gametes were excluded from consideration for testing.

The quality of eggs and sperm was evaluated prior to testing, by adding diluted sperm from each male to eggs from each female in 20 ml of seawater in vials. After ten minutes, eggs were examined under a microscope for the presence of a fertilisation membrane. Combinations of eggs and sperm that did not produce at least 90% fertilisation success were excluded from consideration for testing.

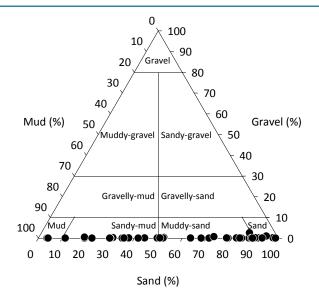
Sperm was activated by exposure to seawater. One hundred microliter aliquots of sperm suspension were then transferred to control (seawater) and elutriates (i.e. supernatant). After ten minutes of sperm exposure, 1 ml of egg suspension was added and left for a further ten minutes. The test was then terminated by adding 100 µl of formalin. Fertilisation success was determined by microscopic examination of an aliquot of the egg suspension from each replicate. Sea urchin gamete sensitivity was assessed using the reference toxicant (positive control) copper, following a similar procedure to that outlined above. Response to the positive control was within an acceptable range.

#### 3. Results and Discussion

#### 3.1. Grain size composition

In a geologically homogenous area, grain size is the single most important factor that controls the natural concentration of metals in sediment. This is because aluminosilicates, the major natural metalbearing phase of sediment, predominate in clay. Sand, in contrast, is comprised largely of metal deficient quartz (silica), and acts as a diluent of metal concentrations. Muddy sediment thus naturally has a higher metal content than sandy sediment. Mud also sequesters metals that are anthropogenically introduced in solution to surface waters because of the large surface area provided by the grains for adsorption and because their surface is electrically charged, rendering them chemically reactive. Metals and other contaminants that are particle reactive also attach to and are transported with suspended particulate matter in the water column, ultimately settling and accumulating in depositional zones. These are areas where the sediment is dominated by fine-grained material (e.g. mud) and form where water currents are so weak the fine-grained suspended material (and any associated contaminants) settles from the water column. As a general rule, therefore, naturally occurring and anthropogenically introduced metal concentrations are highest in muddy sediment and lowest in sandy sediment. There may be exceptions to this general rule in ports since coarse-grained sediment may contain a high metal concentrations due, for example, to the inclusion of metal flecks and metal-impregnated antifouling coating flakes derived from vessel construction and maintenance facilities, or metal ore particles spilled during the loading of vessels.

The grain size composition of sediment thus provides important information for identifying areas in Durban Bay where particle reactive contaminants have the propensity to accumulate. Anomalously high metal concentrations in sandy sediment provides indirect information on the likelihood that the metals are present as a solid (*i.e.* in a largely non-bioavailable form), which has important implications for understanding the toxicological risks posed by the concentrations. Last, the grain size composition of sediment allows an assessment on whether the chosen normaliser



**Figure 3.** Ternary plot illustrating the proportional contribution of gravel, sand and mud to the bulk weight of sediment collected in Durban Bay in June 2018.

for baseline metal concentration model definition (see below) is a reliable proxy for the natural metalbearing phases of the sediment.

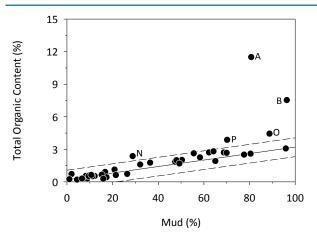
From a textural perspective the sediment at most stations in Durban Bay in June 2018 is classified as muddy-sand or sandy-mud, but that at several stations as sand and at two stations as mud (Figure 3; data in Appendix 3). The dominant grain size class at 20 of the stations was mud, at 11 stations was fine-grained sand, and at ten stations was medium-grained sand. The contribution of mud to the bulk weight of sediment varied widely, but as stated above at only two stations was it so high (≥90%) for the sediment to be classified as mud. These were Station B in the lower part of the Silt Canal and Station 2 at Berth 12 in Congella Basin. All but two of the stations where mud was the dominant grain size class were situated in the upper part of the Bay. Sediment at stations in the lower part was thus always dominated by sand apart from Station 7 at Berth O/P at the T-Jetty and Station 9 at Berth 101/102 at the Pier 1 Container Terminal. Coarse material (i.e. gravel, very coarsegrained sand) was poorly represented, comprising <3% of bulk sediment weight at 30 stations but reaching as high as 10.5% at Station 13 at the Coal Terminal, 7.6% at Station 8 at Berth 107/108 at the Pier 1 Container Terminal, and 6.6% at Station EC in the Entrance Channel.

The findings for the 2018 survey are consistent with

those of previous surveys. The high mud fraction of sediment in the upper part of Durban Bay reflects a combination of factors, including most importantly weak currents that characterise this part of the Bay and the input of mud-sized material via rivers that flow into the Silt Canal, which largely settles from the water column in the upper part (as revealed by turbidity and suspended solids concentrations; CSIR, unpublished data). All things being equal, the high mud fraction in the upper part of the Bay alludes to a greater propensity for the retention and accumulation of particle reactive contaminants than in the lower part. The propensity for contaminant retention is less in the lower part, due to the coarser-grained sediment and distance from the most significant sources of mud-sized material to the Bay.

#### 3.2. Total organic content

Particulate organic matter in sediment provides an additional site for the adsorption of contaminants that have a propensity for adsorbing onto this material, including metals such as cadmium and mercury, and organic contaminants, such as polycyclic aromatic hydrocarbons. Metals and other contaminants that are particle reactive attach to and are transported with suspended particulate matter in the water column, ultimately settling and accumulating in depositional zones. Due to its finegrained nature, particulate organic matter is deposited on and winnowed from sediment concurrently with mud depending on the prevailing current regime. Mud and particulate organic matter tend, therefore, to accumulate in or be depleted from sediment in the same areas. The total organic content of sediment thus provides important information for identifying major sources and depositional zones of particulate organic matter in Durban Bay, and thus for identifying parts of the Bay that are susceptible to the accumulation of contaminants that preferentially adsorb onto this matter. Total organic content is also monitored to determine if the sediment is so enriched with particulate organic matter that its exposure during dredging will likely result in an excessive oxygen demand by microorganisms that degrade this matter. Since dissolved oxygen is a fundamental requirement for the survival of most forms of aquatic life an excessive oxygen demand is of obvious ecological concern.



**Figure 4.** Baseline model for the total organic content in sediment in Durban Bay, with the total organic content in sediment collected in June 2018 superimposed. Selected data are highlighted by station identifiers.

In aquatic ecosystems where there the sediment is not enriched with particulate organic matter from an anthropogenic source there is usually a strong relationship between the mud fraction and total organic content of sediment, due to their similar deposition and winnowing from sediment by prevailing currents. The relationship is beneficial because it can be used to identify sediment with an anomalous total organic content. Scientists from the Coastal Systems research group of the CSIR have defined a baseline model for the total organic content of sediment in Durban Bay using the results from past research and monitoring in the Bay (Figure 4). The baseline model comprises a linear regression and 99% prediction limits (oblique solid and dashed lines in Figure 4). The regression defines the average total organic content at cooccurring mud fractions in sediment at baseline locations in Durban Bay, while the upper and lower prediction limits define the range around the average in which 99% of measurements should fall if the sediment is not enriched with particulate organic matter and the data used to define the model is normally distributed. Data that plot above the upper prediction limit indicate the sediment has a higher than expected total organic content and is deemed to be enriched with particulate organic matter.

Superimposing the total organic content in sediment collected in Durban Bay in June 2018 onto the baseline model identifies the sediment at Stations A and B in the Silt Canal, Station N in Maydon Wharf Channel, and Stations O and P in

Esplanade Channel as enriched with particulate organic matter (Figure 4; data in Appendix 3). Apart from Stations A and B, the enrichment was of a low magnitude. Particulate organic matter enrichment of sediment in the Silt Canal has been a more or less consistent feature of previous surveys. The excess particulate organic matter at Stations A and B is almost certainly introduced by the Umbilo and Umhlatuzana Rivers. This said, some of the particulate organic matter probably also has a source in the port, including senescent microalgae that often reach bloom status in the Silt Canal due to the excessive introduction of nutrients by the rivers. The source of the excess particulate organic matter at Stations N, O and P is uncertain, but its introduction via the Canal Road culvert cannot be excluded considering the proximity of these stations to one another and the culvert (see Figure 2).

The magnitude of enrichment at Stations N, O and P is so low it is unlikely the oxygen demand of aerobic bacteria that will degrade this matter when it is exposed during dredging will significantly depress the dissolved oxygen concentration in the water column at both the dredging and dredged material disposal sites. The disposal site is in a dispersive environment and fine-grained material is rapidly winnowed from the sediment by currents. This conclusion is based on the fact that sediment on the disposal site is dominated by (usually medium-grained) sand and has a low mud and total organic content, even shortly after the disposal of sediment dredged in Durban Bay (CSIR unpublished data). The situation for Stations A and B is different. The sediment at Station A is highly anoxic, and that at Station B to a lesser degree due to the excessive accumulation of particulate organic matter in the sediment and the host of associated issues this leads to). Dredging of the sediment here is likely to result in the depression of the dissolved oxygen concentration in the water column when hydrogen sulphide and ammonia that typically accumulate in anoxic sediment are oxidised, and due to the oxygen demand of aerobic bacteria that degrade organic matter. However, sediment in the Silt canal is rarely dredged. It is unlikely the disposal of sediment dredged at these stations would result in significant dissolved oxygen depression at the disposal site based on the highly dispersive nature of the site, as discussed above.

The findings for the 2018 survey are consistent with those of previous surveys from the perspective that sediment in Durban Bay has typically not been significantly enriched with particulate organic matter apart from in the Silt Canal, where the enrichment was often high.

#### 3.3. Metals

It is easy to determine if sediment is contaminated by certain chemicals since they do not occur naturally in the environment, but are manmade (e.g. polychlorinated biphenyls). The mere presence of these chemicals in sediment indicates it is contaminated. Determining if sediment is metal contaminated is far more complicated. This is because metals are a ubiquitous naturally occurring component of sediment. The mere presence of metals in sediment thus does not automatically imply it is contaminated. Metal concentrations in uncontaminated sediment can also vary naturally by orders of magnitude over a relatively small spatial scale depending on the sediments mineralogy, granulometry and organic content amongst other factors (Loring and Rantala, 1992; Kersten and Smedes, 2002). High metal concentrations in sediment thus also do not automatically imply it is contaminated but may simply reflect the mineralogy of the parent material and its grain size and organic content. As a further complication, in spite of input and transport dissimilarities, naturally occurring and anthropogenically introduced metals tend to accumulate in the same areas (Hanson et al., 1993). As a result of these complexities an identical metal concentration in two sediment samples from the same aquatic system may reflect contamination in one instance but not the other, because of a difference in the grain size and organic content of the sediment. A low metal concentration might reflect contamination but a higher concentration might not for the same reason.

To meaningfully interpret metal concentrations in sediment it is necessary to first compensate for factors that control their natural variation before background or baseline concentrations can be differentiated from enriched (higher than expected) concentrations, which may reflect contamination. This is usually accomplished by the procedure of

geochemical normalisation, wherein metal concentrations are mathematically normalised to a co-occurring conservative element that provides a tracer of crustal decomposition (Hanson *et al.*, 1993; Kersten and Smedes, 2002). The purpose of geochemical normalization is to compensate for the variables that influence the natural variation of metal concentrations in sediment (principally grain size) such that after normalization concentrations in equally contaminated or uncontaminated sediment with a different granulometry do not differ significantly (Kersten and Smedes, 2002).

In a geologically homogenous area, metals tend to be present in uncontaminated sediment in relatively constant proportions (Wedepohl, 1995; Kersten and Smedes, 2002), with their absolute concentration largely controlled by the sediment grain size (Horowitz, 1991; Loring, 1991). There is usually a strong linear relationship between metal concentrations and the silt and clay (mud) fraction, and between concentrations of different metals in sediment. It is these relationships that provide the basis for geochemical normalization, wherein the relationships between a metal and an element that provides a conservative tracer of the natural metalbearing phases of sediment is modelled through simple linear regression analysis (Hanson et al., 1993; Kersten and Smedes, 2002). Simple linear regression models and associated prediction limits that describe the relationship between a metal and co-occurring normaliser are referred to as baseline metal concentration models, or simply baseline models.

In 2011, scientists from the Coastal Systems research group of the CSIR initiated research that had the objective of defining baseline metal concentrations for sediment in Durban Bay. The concentrations of 15 metals were analysed in 129 sediment samples. The concentrations were used to define a baseline model for each metal. The baseline models were refined after analysis of the same metals in a further 89 sediment samples collected in 2012. The models have been refined further as new data for metal concentrations in sediment in the Bay has become available. The procedure used to define the baseline models is too voluminous to discuss in detail in this report. Briefly, concentrations of each metal were plotted

against corresponding aluminium concentrations. A simple linear regression and 99% prediction limits were fitted to the scatter plots. Metal concentrations falling outside the prediction limits were deemed outliers and sequentially trimmed, starting with the concentration with the largest residual, reiterating the regression, and proceeding in this manner until all concentrations fell within the prediction limits. The models represent baseline rather than background concentrations since some concentrations in the models may reflect low magnitude contamination of sediment in Durban Bay.

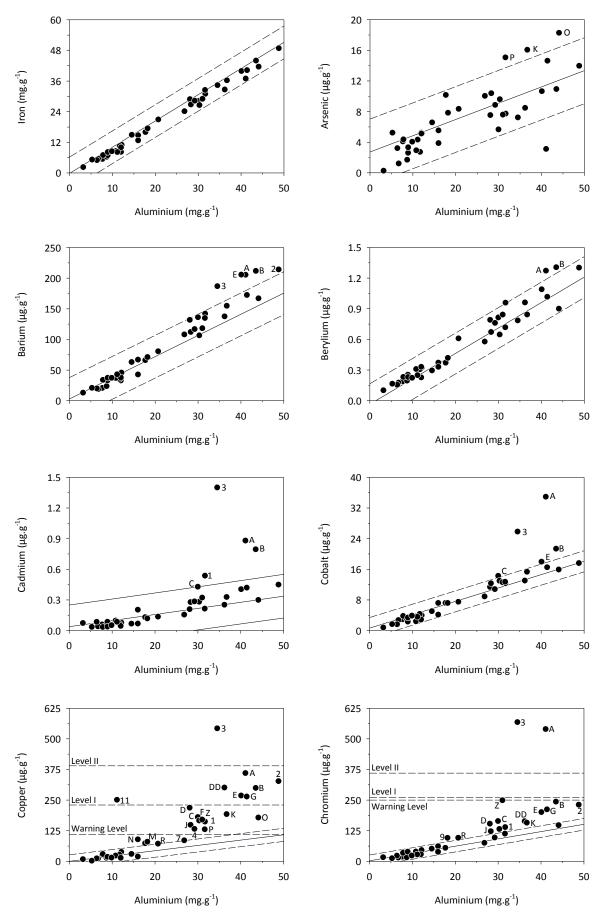
The baseline models are provided in Figure 4, with aluminium normalised metal concentrations analysed in sediment collected in Durban Bay in June 2018 superimposed (data in Appendix 4). Aluminium was used as the normaliser of metal concentrations because it is highly refractory, is structurally combined to one or more of the major metal-bearing phases of sediment, co-varies in proportion to naturally occurring concentrations of other metals, is insensitive to inputs from anthropogenic sources, and is stable and not subject to environmental influences such as reduction/oxidation, adsorption/desorption other diagenic processes that may alter sediment concentrations. Aluminum is used as a proxy for the granulometric variation of sediment, more specifically the variation in the silt and clay (mud) fraction. To demonstrate this point the aluminium concentration in sediment collected in Durban Bay in June 2018 is very strongly positively correlated to the mud fraction (r = 0.980, p < 0.001).

As stated above, the baseline models comprise a regression line and upper and lower 99% prediction limits (oblique and solid and dashed lines in Figures 5 and 6). The regression defines the average concentration for a metal at co-occurring aluminium concentrations in sediment at baseline locations<sup>1</sup> in Durban Bay, while the upper and lower prediction limits define the range in which 99% of concentrations should fall if the sediment is uncontaminated and the concentrations used to define the baseline model are normally distributed.

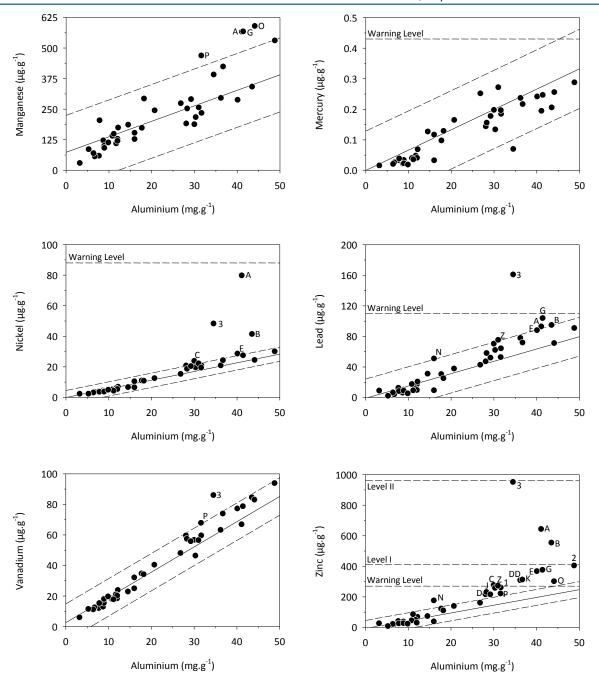
<sup>1</sup> Note that the term baseline location, as used here, does not imply the absence of metal contamination at these locations but rather sediment that appears at most to be minimally metal contaminated.

Metal concentrations that exceed the upper prediction limit when superimposed onto a baseline model indicate the sediment is enriched (see Figure 6). A concentration that exceeds the upper prediction limit does not automatically imply it was enhanced through an anthropogenic contribution but rather that it is atypical of the data used to define the model. Several reasons other than an anthropogenic input can result in a metal concentration exceeding the upper prediction limit. These include analytical variability and errors, poor model assumptions, the probability that metal concentrations in some samples will naturally exceed the upper prediction limit (in a normally distributed population, at the 99% prediction limit one in every 100 concentrations could conceivably naturally exceed the limit), and natural enrichment not captured by the baseline data set (Schropp et al., 1990; Rae and Allen, 1993). Interpretation of enrichment, and ultimately whether this reflects contamination thus requires consideration of ancillary factors, including possible biogeochemical processes that may lead naturally to metal enrichment, the absolute difference between a metal concentration and upper prediction limit, the location of enriched sediment relative to known or potential anthro-pogenic sources of metals, and an assessment of the number of metals in a sediment sample that exceed upper prediction limits. The the difference larger between metal concentration and upper prediction limit (see Figure 6) and the greater the number of metals enriched in a sediment sample the greater the likelihood they reflect contamination. This is because sediment in ports is usually enriched by several rather than a single metal, particularly if anthropogenic sources are diffuse (e.g. stormwater runoff). This said, enrichment of sediment in a port by a single metal may occur, such as in areas where metal ore is exported and there are few other anthropogenic sources of metals in the area. However, even in these cases other metals may be enriched in the sediment as they are usually impurities of the ore.

The concentrations of most metals in sediment at most stations in Durban Bay in June 2018 fall within baseline model prediction limits, that is, they are within the expected baseline range for sediment in the Bay (Figure 5).



**Figure 5.** Baseline metal concentration models for sediment in Durban Bay, with metal concentrations in sediment collected in June 2018 superimposed. Sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal are included if they fall within the y-axis range. Some metal concentrations are highlighted by station identifiers.



**Figure 5 continued.** Baseline metal concentration models for sediment in Durban Bay, with metal concentrations in sediment collected in June 2018 superimposed. Sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal are included if they fall within the y-axis range. Some metal concentrations are highlighted by station identifiers.

The concentrations of one or more metals in the sediment at numerous stations did, however, exceed baseline model upper prediction limits, in some cases significantly. The sediment with the highest number of metals (ten) at an enriched concentration was at Station A in the Silt Canal, off the inflow of the Umbilo/ Umhlatuzana Rivers (Figures 7 and 8). The next highest was nine metals at Station B, also in the Silt Canal, and at Station 3 at Berth 9/10 in Maydon Wharf Channel, followed by six metals at Station C, again in the Silt Canal,

and at Station E off the Ship Repair Jetty in Congella Basin. The highest, or amongst the highest number of metals at an enriched concentration was also found in sediment at these stations in previous surveys (see further below). The sediment at all stations in the Silt Canal and Congella Basin, and at most stations in Maydon Wharf and Esplanade Channels was enriched by at least one metal, but the number enriched was typically higher in the Silt Canal and Congella Basin (Figures 7 and 8). Sediment at only three stations (Stations 7, 9 and

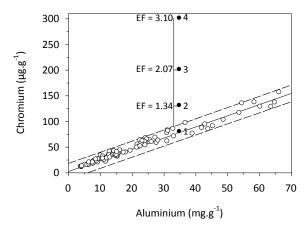
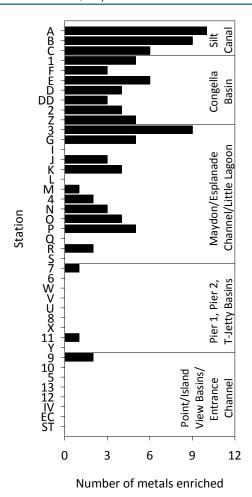


Figure 6. Baseline model for chromium in sediment in Durban Bay. Open symbols represent concentrations that define the baseline model, while numbered solid symbols represent four hypothetical scenarios: 1. concentration is within baseline model prediction limits (dashed lines) and is not enriched; 2, 3 and 4. concentrations exceed baseline model upper prediction limit and reflect various degrees of enrichment broadly defined as low (2) to high (4). Situations 3 and 4 would be interpreted as reflecting contamination with a high level of confidence. Enrichment Factors (EF) for three of the scenarios are provided.

11) in the lower part of the Bay, taking Station R as separating the upper and lower parts (see Figure 2), was enriched by one or two metals.

Copper was the most frequently enriched metal, at a higher than expected concentration in sediment at 23 of the 41 stations, followed by zinc at 18 stations, chromium at 16 stations, and nickel at seven stations (Figures 6 and 9). These have been the, or amongst the most frequently enriched metals in sediment in the Bay in previous surveys (see further below). Iron and mercury were never at an enriched concentration, while arsenic was enriched at two stations and beryllium and manganese at three stations each (Figures 6 and 9). These have been the, or amongst the least frequently enriched metals in sediment in the Bay in previous surveys (see further below).

Assessing metal contamination of sediment by counting the number of metals at a concentration exceeding baseline model upper prediction limits provides important information. This is because sediment in ports is rarely contaminated by a single metal, due to the multitude of anthropogenic sources of metals in and to these environments. Thus, as stated above the greater the number of metals enriched in sediment the more likely the



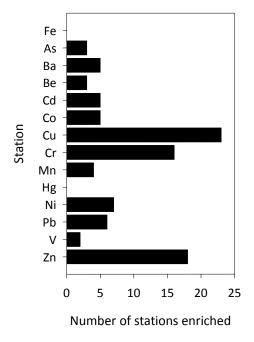
**Figure 7.** The number of metals enriched in sediment collected in Durban Bay in June 2018. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station ST at the eastern most part of the south breakwater in the entrance channel (see Figure 2).

excess metal concentrations were the result of anthropogenic inputs. However, a count of the number of metals enriched does not contextualise the magnitude of enrichment. There are only two possibilities in this approach, namely the sediment is either metal enriched or it is not enriched, and the same weight is thus given to sediment enriched by the same number of metals. However, the magnitude of enrichment may be very different, with very different toxicological and management implications.

To contextualise the magnitude of enrichment an Enrichment Factor (EF) was calculated for each metal concentration. Metal concentrations were first adjusted to the average aluminium concentration for the baseline model, using the model parameters. This was done to avoid anomalous Enrichment Factors that are the result



**Figure 8.** Bubble plot illustrating the number of metals enriched in sediment collected in Durban Bay in June 2018. The bubbles are scaled to show differences between stations.



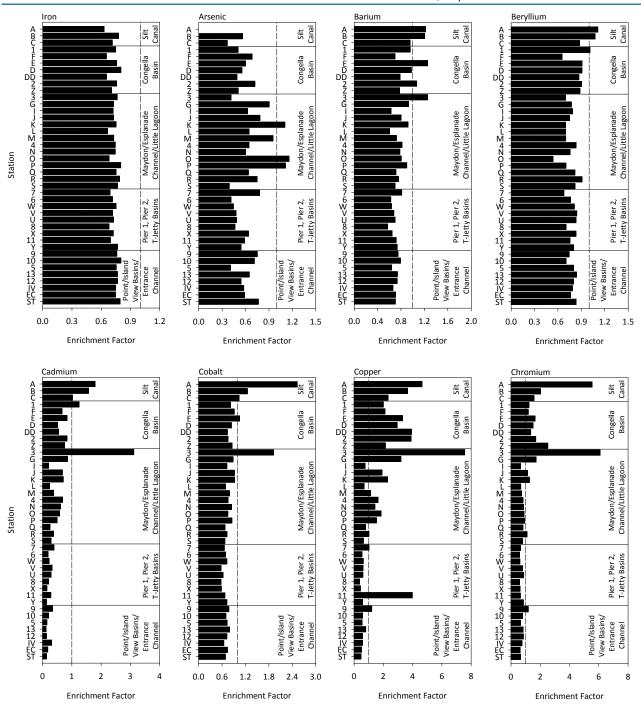
**Figure 9.** The number of stations in Durban Bay where sediment collected in June 2018 was enriched by various metals.

of the baseline models not having a zero intercept or a slope of unity, which results in ratio distortion across the normalisation range. The Enrichment Factor was then taken as the ratio between the metal concentration in a sediment sample and the concentration predicted at the baseline model upper prediction limit. The upper prediction limit of the baseline model for each metal was thus used to

discriminate between enriched and non-enriched sediment and represents the highest concentration expected in sediment at baseline locations.

The Enrichment Factor, which is unitless, indicates how many times a metal concentration exceeds the concentration predicted at the baseline model upper prediction limit. An Enrichment Factor ≤1 indicates the concentration is lower than the predicted concentration while an Enrichment Factor >1 indicates the concentration exceeds the predicted concentration. Enrichment Factors can be visualised using the same hypothetical example to show how baseline models are used to interpret metal concentrations in sediment (Figure 6). The Enrichment Factor for hypothetical concentrations 2, 3 and 4 increases since they exceed the baseline model upper prediction limit by an increasing amount. The Enrichment Factor for hypothetical concentration 4 is 3.10, meaning the concentration was a little over three times higher than the concentration predicted at the baseline model upper prediction limit.

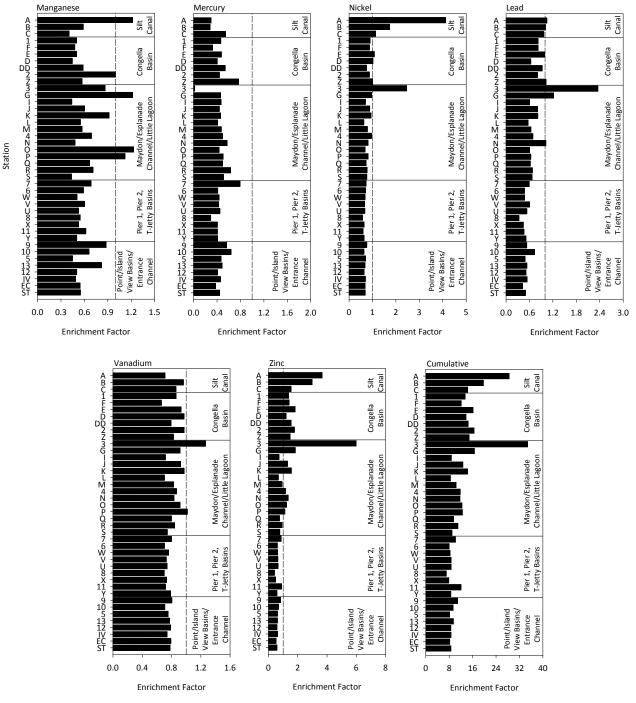
As expected from the above comparison of metal concentrations to the baseline models, the Enrichment Factor for most metals in sediment collected at most stations in Durban Bay in June 2018 was ≤1 (Figure 10).



**Figure 10.** Enrichment Factors for metals in sediment collected in Durban Bay in June 2018. The vertical dashed lines represent an Enrichment Factor = 1. Enrichment Factors >1 indicate the metal was at a higher than expected concentration and may indicate contamination. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station ST at the eastern most part of the south breakwater in the entrance channel (see Figure 2).

However, the Enrichment Factor for one or more metals at numerous stations was >1, in some cases significantly. Enrichment Factors >1 for some metals are presented as bubble plots in Figure 11, to facilitate interpretation. To create the bubbles the Enrichment Factors were constrained to values between zero and one. The bubbles are thus not directly comparable between metals, but the plots provide an understanding on where the highest

Enrichment Factors for any particular metal were found. The highest Enrichment Factor was 7.6 for the copper concentration in sediment at Station 3 at Berths 9/10 in Maydon Wharf Channel, followed by 6.1 for the chromium concentration and 6.0 for the zinc concentration in the sediment at this same station (Figures 10 and 11). In other words, the concentrations are about 7.5, 6 and 6 times greater than the highest concentration expected at

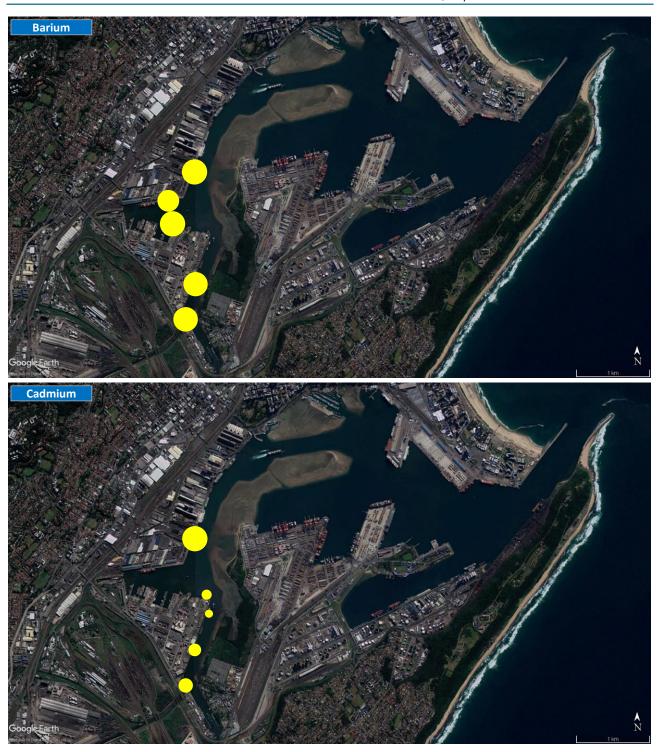


**Figure 10 continued.** Enrichment Factors for metals in sediment collected in Durban Bay in June 2018. The vertical dashed lines represent an Enrichment Factor = 1. Enrichment Factors >1 indicate the metal was at a higher than expected concentration and may indicate contamination. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station ST at the eastern most part of the south breakwater in the entrance channel (see Figure 2).

baseline locations in the Bay. The highest Enrichment Factors were usually for sediment in the Silt Canal and Congella Basin, and at Station 3 at Berths 9/10 in Maydon Wharf Channel. Enrichment Factors for copper and zinc in sediment at each station in the Silt Canal and Congella Basin were >1 (Figures 10 and 11). As discussed above, virtually no metals were enriched in sediment in the lower part of the Bay, but when so the Enrichment Factor was

low (i.e. low magnitude enrichment) apart from copper at Station 11 at the Pier 1 Container Terminal, where the Enrichment Factor was 4.0.

The Cumulative Enrichment Factor, the sum of Enrichment Factors for each metal in sediment at a station provides further understanding on metal enrichment of sediment. From this perspective the most metal contaminated sediment was (in order)



**Figure 11.** Bubble plot illustrating Enrichment Factors for barium (top) and cadmium (bottom) concentrations in sediment collected in Durban Bay in June 2018. The bubbles are scaled to show differences between stations. The largest bubble for arsenic represents an Enrichment Factor of 1.3 and for barium an Enrichment Factor of 3.1.

at Station 3 at Berth 9/10 in Maydon Wharf Channel, Stations A and B in the Silt Canal, Station G at Little Lagoon, and Stations D and 2 in the Congella Basin (Figure 10).

The Enrichment Factors reveal that the most metal contaminated sediment in Durban Bay in June 2018 was in the Silt Canal, Congella Basin, and part of Maydon Wharf Channel. Anthropogenic sources of

metals in Congella Basin undoubtedly include vessel construction and maintenance operations. Copper and zinc, and indeed many other metals are used in some way on vessels. Copper, and to a lesser degree zinc, are for example the most important metal biocides in antifouling coatings on vessel hulls. The grinding and sandblasting of metal structures and hulls on vessels is bound to introduce metal fragments and metal impregnated



**Figure 11 continued.** Bubble plot illustrating Enrichment Factors for cobalt (top) and copper (bottom) concentrations in sediment collected in Durban Bay in June 2018. The bubbles are scaled to show differences between stations. The largest bubble for arsenic represents an Enrichment Factor of 2.5 and for barium an Enrichment Factor of 7.6.

antifouling coating flakes into adjacent waters, particularly if maintenance is performed on floating docks (which is largely the case in Durban Bay) and there is inadequate waste control. The inclusion of copper and zinc impregnated antifouling coating flakes in the sediment may account for much or all of the copper and zinc contamination in Congella Basin, and would also account for the often large variation in metal contamination of sediment at

stations in the basin separated by a relatively short distance.

Research by scientists from the Coastal Systems research group of the CSIR has revealed that the Amanzimnyama, Umbilo and Umhlatuzana Rivers are important vectors for the introduction of anthropogenic metals (and other contaminants) to Durban Bay, but especially to the Silt Canal. Metal



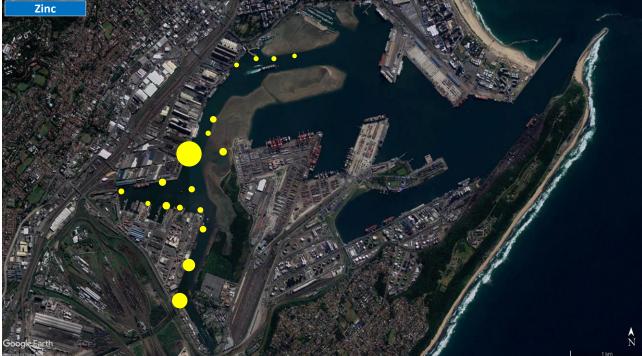
**Figure 11 continued.** Bubble plot illustrating Enrichment Factors for chromium (top) and nickel (bottom) concentrations in sediment collected in Durban Bay in June 2018. The bubbles are scaled to show differences between stations. The largest bubble for arsenic represents an Enrichment Factor of 6.1 and for barium an Enrichment Factor of 4.1.

inputs via these rivers probably accounts for much of the metal contamination of sediment in the Silt Canal.

Based on the findings of monitoring in ports in other parts of the world, surface runoff (stormwater) is probably an important vector for the introduction of anthropogenic metals to Durban Bay. It is, however, not possible to discern the significance of this vector relative to other vectors and anthropogenic sources in the Bay with the data at hand.

The source of the metals in sediment at Station 3 at Berths 9/10 in Maydon Wharf Channel is uncertain, but as discussed further below there is clearly a





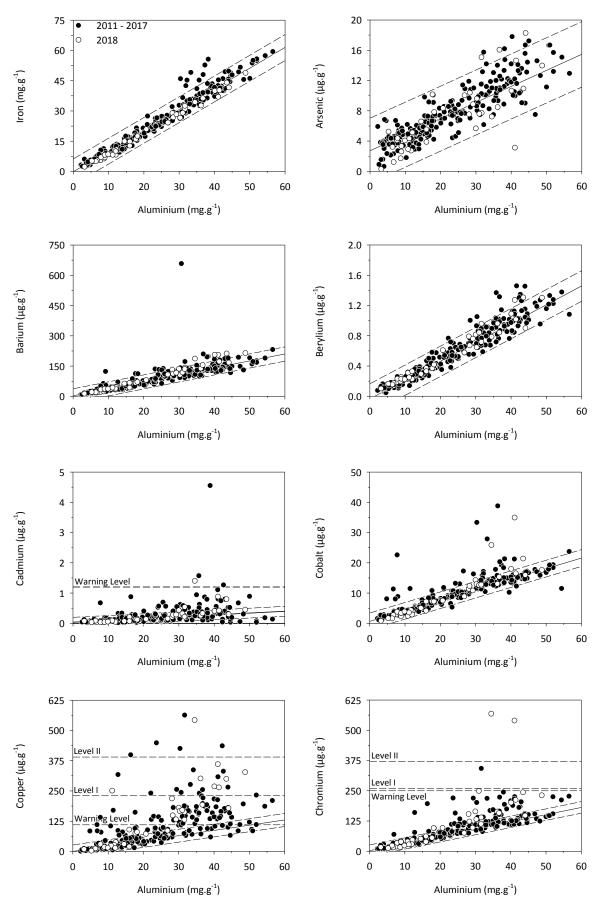
**Figure 11 continued.** Bubble plot illustrating Enrichment Factors for lead (top) and zinc (bottom) concentrations in sediment collected in Durban Bay in June 2018. The bubbles are scaled to show differences between stations. The largest bubble for arsenic represents an Enrichment Factor of 2.4 and for barium an Enrichment Factor of 9.0.

persistent and significant source of metals in this area of Durban Bay.

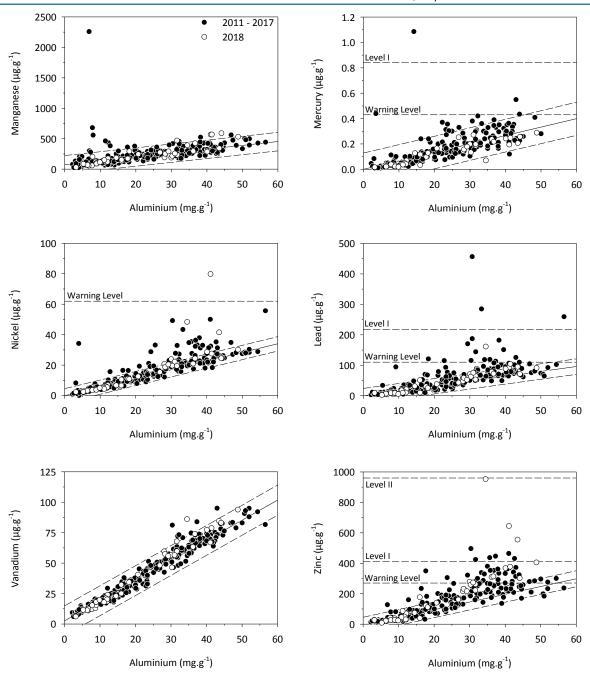
# 3.4. Historical trends for metal concentrations

In monitoring programmes that involve the collection of data at frequent intervals and/or over a long period there is both an interest and a need

to compare trends between surveys. If various chemicals that found to be contaminants of sediment between surveys, and the frequency of contamination at any station is consistent this indicates there are consistent anthropogenic sources of contaminants to the system. An increase in the number of chemicals that are contaminants or a change in the frequency of contamination



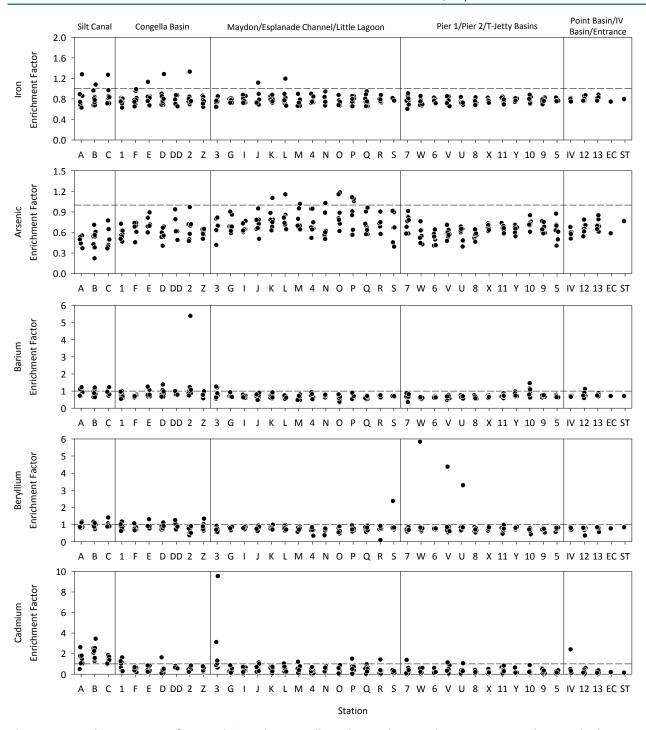
**Figure 12.** Baseline metal concentration models for sediment in Durban Bay, with metal concentrations in sediment collected between 2011 and 2018 superimposed. Sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal are included when they fall within the y-axis range.



**Figure 12 continued.** Baseline metal concentration models for sediment in Durban Bay, with metal concentrations in sediment collected between 2011 and 2018 superimposed. Sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal are included when they fall within the y-axis range.

identifies new sources or increased inputs of contaminants. Inter survey comparisons are also important for identifying if strategies implemented to control contaminant inputs are proving effective. Metal concentrations analysed in sediment collected in Durban Bay in surveys between 2011 and 2018 are compared to the baseline models in Figure 12. Enrichment Factors for metal concentrations and the number of metals enriched in sediment at each station over this period are provided in Figures 13 and 14. The sediment at numerous stations in the upper part of the Bay was

enriched by one or more metals in all or most surveys. For example, in each survey the sediment at Station B was enriched by cadmium while that at Stations D, DD and E in Congella Basin and Station 3 in Maydon Wharf Channel was enriched by copper. The number of metals enriched in sediment has varied widely between surveys at numerous stations in the upper part of the Bay. For example, the number of metals enriched in sediment at Station A off the inflow of the Umbilo/Umhlatuzana Rivers has ranged from one to 11, and at Station 2 in Congella Basin from zero to nine. The difference

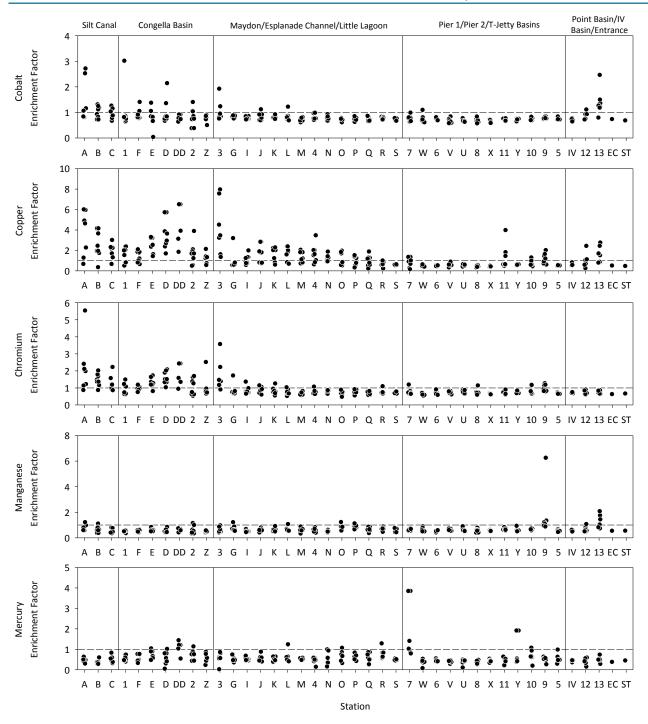


**Figure 13.** Enrichment Factors for metals in sediment collected in Durban Bay between 2011 and 2018. The horizontal dashed lines represent an Enrichment Factor = 1. Enrichment Factors >1 indicate the metal was at a higher than expected concentration and may indicate contamination. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station ST at the eastern most part of the south breakwater in the entrance channel (see Figure 2).

in the magnitude and frequency of metal enrichment of sediment at many stations between surveys probably reflects differences in the grain size of sediment sampled, small spatial scale and temporal variability in the presence of metal flecks, metal impregnated antifouling coating flakes and metal ore particles in sediment, variable anthropogenic inputs of metal contaminants, and the removal of contaminated sediment by dredging

amongst other factors. The repeated or frequent enrichment of sediment at certain stations points to persistent anthropogenic sources of metals in and to the relevant parts of Durban Bay.

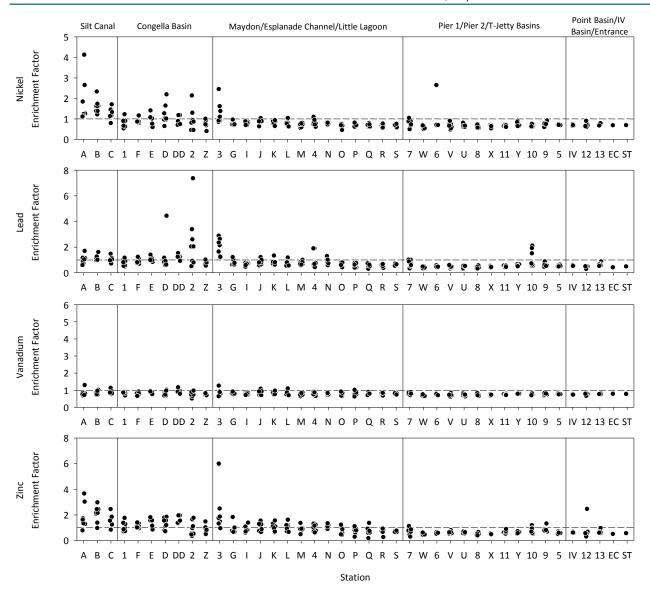
Metal enrichment of sediment in the lower part of Durban Bay was far less common, but some interesting trends are evident. Copper has been a fairly common contaminant of sediment at Station 11 at Berth 104 at the Pier 1 Container Terminal.



**Figure 13 continued.** Enrichment Factors for metals in sediment collected in Durban Bay between 2011 and 2018. The horizontal dashed lines represent an Enrichment Factor = 1. Enrichment Factors >1 indicate the metal was at a higher than expected concentration and may indicate contamination. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station ST at the eastern most part of the south breakwater in the entrance channel (see Figure 2).

Several metals have been common contaminants of sediment at Station 13 at the Coal Terminal, including cobalt, copper and manganese. This probably reflects the spillage or ingress by other means of these metals during their periodic export in concentrate form through this part of the port. Lead has been a fairly common contaminant of sediment at Station 10 at Berth M at the T-Jetty.

The highest, or amongst the highest cobalt, copper, chromium, nickel and zinc concentrations measured in sediment in Durban Bay since 2011 were for sediment collected in 2018. This was, however, restricted to one or two stations and from an overall perspective the magnitude of enrichment in 2018 was not inordinately different to that for surveys since 2011. The spatial extent of enrichment was, however, more extensive than in



**Figure 13 continued.** Enrichment Factors for metals in sediment collected in Durban Bay between 2011 and 2018. The horizontal dashed lines represent an Enrichment Factor = 1. Enrichment Factors >1 indicate the metal was at a higher than expected concentration and may indicate contamination. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station ST at the eastern most part of the south breakwater in the entrance channel (see Figure 2).

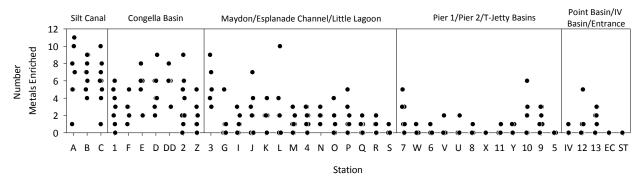
certain previous surveys, mainly due to the metal enrichment of sediment at numerous stations in Maydon Wharf and Esplanade Channel.

#### 3.5. Organic chemicals and tributyltin

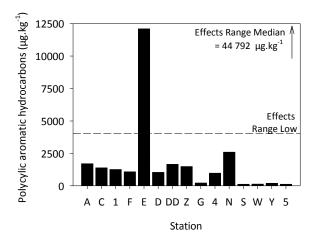
Polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls and butyltins were analysed in sediment collected at between 12 to 15 stations in Durban Bay in June 2018. This is obviously far fewer stations than the number of stations (41) where the sediment was analysed for metals. The results do not thus provide as comprehensive an understanding of the spatial extent of contamination, or lack thereof compared to metals, but is nevertheless very useful for

identifying if these chemicals are important contaminants of sediment in the Bay.

Polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls and butyltins are common and often significant contaminants of sediment in other South African ports, and in ports in other parts of the world, and pose significant direct or indirect ecological and human health risks. However, these chemicals are not used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal. The decision to analyse sediment collected in Durban Bay in June 2018 for these metals was thus made



**Figure 14.** Number of metals enriched in sediment collected in Durban Bay between 2011 and 2018. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station ST at the eastern most part of the south breakwater in the entrance channel (see Figure 2).



**Figure 15.** Total polycyclic aromatic hydrocarbon concentrations in sediment collected in Durban Bay in June 2018. The Effects Range Low of the Long *et al.* (1995) sediment quality guidelines is represented by the horizontal dashed line. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station 5 in Point Basin in the lower part (see Figure 2).

on a duty of care basis by Transnet National Ports Authority.

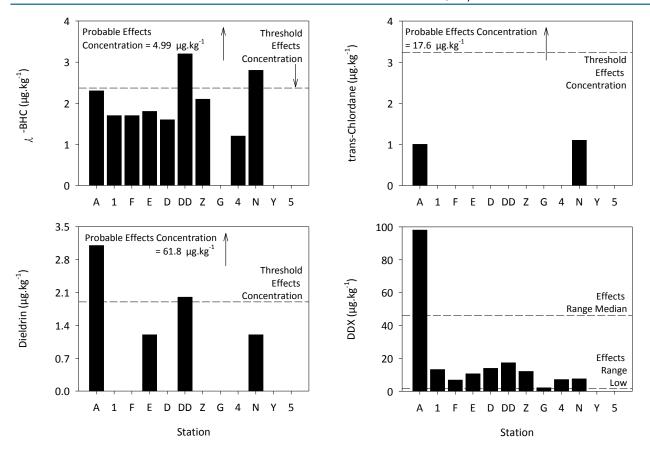
Polycyclic aromatic hydrocarbons are chemicals characterised by two or more fused benzene (aromatic) rings (Neff, 1979). There are two main sources of polycyclic aromatic hydrocarbons to the environment, namely fossil fuels, including refined and unrefined crude oil, and the incomplete combustion of organic matter such as wood, coal and oil (Boehm, 2006). Although there are natural sources of polycyclic aromatic hydrocarbons, such as forest fires, oil seeps, coal and organic matter degradation (Neff, 1979; Hites *et al.*, 1980; Stillman *et al.*, 1998; Baumard *et al.*, 1999; Lima *et al.*, 2005), anthropogenic sources are more significant. The incomplete combustion of wood, coal and

petroleum related products are regarded as the most significant anthropogenic sources of polycyclic aromatic hydrocarbons (McCready *et al.*, 2000; Mahler *et al.*, 2005; Boehm, 2006; Mostert *et al.*, 2010).

Polycyclic aromatic hydrocarbons are generally hydrophobic and have a high octanol/water coefficient, and thus preferentially partition to suspended particulate material in the water column and more commonly to sediment (Karickhoff *et al.*, 1979; Means *et al.*, 1980; Douben, 2003). As a result, polycyclic aromatic hydrocarbons released into the aquatic environment often have limited potential to occur in dissolved form, or if they are present in water it is only for a short time. Sediment is the most important sink and reservoir for these chemicals in the aquatic ecosystem, with concentrations usually orders of magnitude higher than in the water column.

Polycyclic aromatic hydrocarbons are of ecological and human health concern since some are known or strongly suspected carcinogens and mutagens (IARC, 1991; Luch, 2005). In general, low molecular weight (two and three ring) isomers display significant acute toxicity while high molecular weight (four to seven ring) isomers display greater carcinogenicity. Due to toxicological concerns, the United States Environmental Protection Agency identified sixteen polycyclic aromatic hydrocarbons as priority pollutants (Keith and Telliard, 1979; see review by Xue and Washarsky, 2005).

Twenty polycyclic aromatic hydrocarbon isomers were analysed in sediment collected at 15 stations in Durban Bay in June 2018. However, this discussion focusses only on the total concentration,

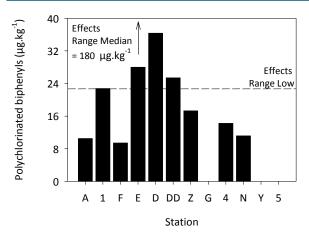


**Figure 16.** Organochlorine pesticide concentrations in sediment collected in Durban Bay in June 2018. The Effects Range Low and Effects Range Median of the Long *et al.* (1995), and Threshold Effects Concentration of the MacDonald *et al.* (2000) sediment quality guidelines are represented by horizontal dashed lines. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station 5 in the Point Basin in the lower part (see Figure 2).

that is, the sum of all isomer concentrations. Polycyclic aromatic hydrocarbons were concentration above the method detection limit in each sediment sample, but not necessarily each isomer (Figure 13; data in Appendix 6). By far the highest concentration was in sediment at Station E at the Ship Repair Jetty in Congella Basin. Concentrations at Stations 1, F, D, DD and Z, also in Congella Basin, and at Stations A and C in the Silt Canal were relatively high. There was a high degree of variation in the concentration between stations in close proximity in Congella Basin. For example, Stations D and E in Congella Basin were separated by about 180 m, yet there was an almost 12 fold difference in concentration. The reason is uncertain, but must, in part, reflect a highly localised input and/or mechanism for the retention of polycyclic aromatic hydrocarbons in sediment in specific areas of this basin. The periodic removal of contaminated sediment by dredging also cannot be discounted. The concentration at Station G at Little Lagoon was low.

The lowest concentration was in sediment at Station S in the intertidal near the Point Yacht Club basin (Figure 13). This was expected since the sediment in this part of the intertidal in Durban Bay is dominated by sand, which has a low contaminant retentive capacity. The concentration in sediment at Stations W and Y in the Pier 1 and 2 Container Terminal basin and Station 5 in the Point Basin was far lower than that at most stations in the upper part.

As stated above, polycyclic aromatic hydrocarbons preferentially adsorb onto fine-grained material, such as mud and particulate organic matter. Total polycyclic aromatic hydrocarbon concentrations and the mud fraction of sediment were strongly positively correlated (r = 0.949, p < 0.001) provided the data for Stations E and N are considered outliers. In contrast, the relationship with the total organic content was weak, even after the trimming of clear outliers. The strong correlation for mud suggests the polycyclic aromatic hydrocarbons are partitioning mainly to this phase of the sediment

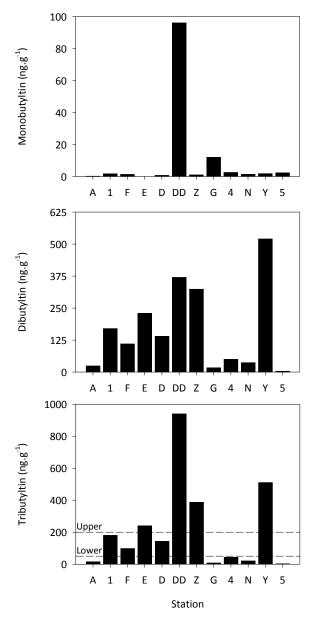


**Figure 17.** Total polychlorinated biphenyl concentrations in sediment collected in Durban Bay in June 2018. The Effects Range Low of the Long *et al.* (1995) sediment quality guidelines is represented by the horizontal dashed line. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station 5 in the Point Basin in the lower part of the Bay (see Figure 2).

and are somewhat diffuse in source, apart from the two outliers. These seem to reflect a significant localised input and accumulation of these chemicals in these areas.

The sum of high molecular weight isomer concentrations was far higher than that for the sum low molecular weight concentrations in sediment at all stations. This reflects in part that high molecular weight isomers are more hydrophobic than low molecular weight isomers and thus preferentially accumulate in sediment while lower molecular weight isomers are more soluble, but probably also that the polycyclic aromatic hydrocarbons were relatively old (weathered).

The total higher polycyclic aromatic hydrocarbon concentrations in sediment in the Silt Canal, Congella Basin and Maydon Wharf Channel probably reflect a complex interplay of factors, including proximity to significant anthropogenic sources of these chemicals in and to the port (e.g. vessel maintenance facilities, stormwater outfalls) and the high mud fraction and total organic content of the sediment. The weak currents that characterise the upper part of the Bay facilitate the settlement of particle-reactive chemicals from the water column. Although polycyclic aromatic hydrocarbons were analysed in fewer samples than metals a similar trend is apparent in that contamination of sediment in the upper part of the



**Figure 18.** Butyltin concentrations in sediment collected in Durban Bay in June 2018. The horizontal dashed lines represent OSPAR (2011) sediment quality guidelines. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station 5 in the Point Basin in the lower part of the Bay (see Figure 2).

Bay was more pronounced than in the lower part. This is supported by other research in Durban Bay by scientists from the Coastal Systems research group of the CSIR (unpublished data). The low concentrations in sediment in the lower part probably reflect that the sediment here has a low mud fraction, and possibly also a lower anthropogenic input and/or their more efficient dispersion and flushing from the Bay.

Organochlorine pesticides are often referred to as legacy contaminants since their production and use has been banned or restricted under the conditions

of the Stockholm Convention on Persistent Organic Pollutants. For example, DDT is still used to control malaria-bearing mosquitoes in some parts of South Africa, including northern KwaZulu-Natal, but its use as an agricultural pesticide is banned. Many organochlorine pesticides are persistent in the environment as a result of their chemical stability, explaining their listing under the Stockholm Convention. They remain in the environment for long periods after release. Many are also highly toxic, the primary reason their production and use was banned. They also have a high biomagnification potential. Under persistent exposure, higher trophic level aquatic organisms (e.g. predatory fish) may accumulate such high concentrations of these pesticides in their tissue that this poses a risk to the health of humans that eat fish from contaminated systems.

Four of the 22 organochlorine pesticides and/or their metabolites analysed were detected in sediment collected in Durban Bay in June 2018, namely y-Benzene hexachloride (commonly known as Lindane), trans-Chlordane, Dieldrin, and DDT and its metabolites DDE and DDD (Figure 14, data in Appendix 5). They were only found in sediment in the upper part of the Bay. DDX was most detected most often (at 10 of 14 stations), followed by Lindane (9 stations), Dieldrin (4 stations) and trans-Chlordane (2 stations). Although pesticides were analysed in fewer samples than metals a similar trend is apparent in that contamination of sediment in the upper part of the Bay was more pronounced than in the lower part. The difference probably reflects a complex interplay of factors, including the hydrodynamic regime, nature of the sediment, and proximity to anthropogenic sources of these contaminants in the upper part of the Bay.

DDT and its metabolites have routinely been found in sediment in Durban Bay in previous surveys, but the other pesticides less often (see further below). DDT and its metabolites are in fact common contaminants of sediment in rivers, canals and estuaries in the Durban area and were present at high concentrations in some rivers that flow into Durban Bay in 2011 and 2012 (CSIR, unpublished data). The source of the DDT is uncertain, particularly since the use of this pesticide in South Africa is banned apart from certain controlled uses.

It has been hypothesised that the presence of DDX in the Durban area might reflect its atmospheric transport from the malaria belt in northern KwaZulu-Natal, where DDT is used to control malaria-bearing mosquitoes (Batterman *et al.* 2008). However, this is unlikely as DDT and its metabolites are very uncommon contaminants of sediment in Richards Bay, intermediate between Durban and the malaria belt. This suggests there are still sources of DDT in the Durban area.

The source of Lindane, Dieldrin and trans-Chlordane is also uncertain, but they have also been found in sediment in rivers, canals and estuaries in the Durban area, some of which flow into Durban Bay (CSIR, unpublished data).

Polychlorinated biphenyls were historically used extensively as insulating fluids in electrical transformers, capacitors and other heat transfer devices, as lubricants in compressors, and as plasticisers in paints and rubber sealants (ATSDR 2000). They resist thermal and other degradation processes, reflecting their commercial application where chemical stability was required from a safety, operation and durability perspective. This means, however, that they are also stable and persistent in the environment. The manufacture and use of polychlorinated biphenyls in the United States of America, the largest producer of these chemicals, was banned in 1979, and elsewhere in the world via the Stockholm Convention on Persistent Organic Pollutants in 2001, due to toxicological concerns. Polychlorinated biphenyls have a particularly high biomagnification potential and are listed as probable carcinogens. As is the case with pesticides, under persistent exposure, higher trophic level aquatic organisms predatory fish) may accumulate such concentrations of these chemicals in their tissue that this poses a risk to the health of humans that eat fish from contaminated systems. Despite a ban on their production and restrictions on their use, due to their persistence polychlorinated biphenyls continue to pose ecological and human health risks in many parts of the world (e.g. Baars et al., 2004; Diamanti-Kandarakis et al., 2009; Stahl et al., 2009; Blocksom et al., 2010). In the United States of America, for example, polychlorinated biphenyls are responsible for the most fish consumption advisories after mercury (USEPA, 2011).

Polychlorinated biphenyls were produced by the chlorination of a biphenyl molecule. Between one to ten chlorines were substituted on the biphenyl molecule to create 209 possible congeners, the term used to distinguish polychlorinated biphenyl compounds with unique combinations of attached chlorine. In practice, however, there were about 100 - 150 congeners in polychlorinated biphenyl The congeners have formulations. different biological activity and toxicity. The so-called dioxinlike congeners exert a wide range of toxic responses particularly focused on the endocrine system, while the ortho-substituted congeners seem to produce neurotoxic effects (Rice and Hayward, 1997).

Polychlorinated biphenyls are hydrophobic and preferentially partition to sediment. Sediment is thus the most important sink and reservoir for these chemicals in aquatic ecosystems, with concentrations usually orders of magnitude higher than in the water column.

Although twenty-one polychlorinated biphenyl congeners were analysed in sediment in Durban Bay in June 2018, this discussion focusses only on the total concentration. As stated above there are 209 possible congeners, although all are rarely (if ever) found in environmental samples. Since only congeners were analysed the concentration would likely have been higher if a larger number were analysed. The sum of the 18 so-called National Oceanic and Atmospheric Administration congeners, namely PCB's 8, 18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 153, 170, 180, 187, 195, 206, 209, is often multiplied by a factor of 2.19 to estimate the total polychlorinated biphenyl concentration when a small set of congeners are analysed (as per Lauenstein and Cantillo, 1993). This approach was followed for this survey.

Polychlorinated biphenyls were at a concentration above the method detection limit in nine of the 14 sediment samples in which they were analysed, although not all congeners (Figure 15; see data in Appendix 5). The highest concentrations were in sediment at Stations 1, E, D and DD, all in Congella Basin. Polychlorinated biphenyls were only found in

sediment in the upper part of the Bay. Thus, although polychlorinated biphenyls were analysed in fewer samples than metals a similar trend is apparent, namely contamination of sediment in the upper part of the Bay was more pronounced than in the lower part. The difference probably reflects a complex interplay of factors, including the hydrodynamic regime, nature of the sediment, and proximity to anthropogenic sources of these contaminants in the upper part of the Bay. Although the anthropogenic sources polychlorinated biphenyls in and to Durban Bay cannot be definitively identified, it is possible that in Congella Basin they were derived from vessel maintenance and construction facilities. The common presence of polychlorinated biphenyls in sediment at Station 4 in Maydon Wharf Channel near the Canal Road culvert suggests surface (stormwater) runoff may be a vector for the introduction of these chemicals to Durban Bay. Research by scientists from the Coastal Systems research group of the CSIR in the eThekwini area has shown that polychlorinated biphenyls are present in sediment in many canals, rivers and estuaries in the Durban area (CSIR unpublished data). This probably accounts for the presence of these chemicals at Station A off the inflow of the Umbilo/Umhlatuzana Rivers.

Butyltins are arguably the most ubiquitous, and amongst the most problematic contaminants in sediment in ports and other sheltered waterbodies characterised by maritime activities. This reflects the historical use of tributyltin as the active agent in antifouling coatings applied to vessel hulls and underwater structures to limit the growth of encrusting ('fouling') organisms such as barnacles, and the persistence of tributyltin and its degradation products in sediment. Tributyltin is highly effective in controlling the fouling of vessel hulls and other structures due to its broad spectrum toxicity (Oceanica Consulting 2005). However, this toxicity had unintended consequences for non-target organisms. This was first elucidated by Alzieu et al. (1986), who show a link between exposure to tributyltin and shell thickening in the Pacific oyster Crassostrea gigas. In fact, tributyltin was implicated in the virtual collapse of the oyster culture industry in some parts of France in the 1980's. Subsequent research has

provided numerous examples of the toxicity of tributyltin, including imposex (super-imposition of male characters onto females, an endocrine disruption effect) in a wide variety of gastropods and shell thickening in other bivalves (e.g. Reitsema and Spickett, 1999; Noller, 2003; Reitsema et al., 2003; Anderson, 2004; Bellas et al., 2005; Qiu et al., 2011). Tributyltin has also been implicated in endocrine disruption in fish, including a reduction in reproductive capacity and sexual development. Tributyltin is not only used in antifouling coatings but also as a herbicide and fungicide, as a wood preservative, and for the manufacture polyvinylchloride plastics (Blunden et al., 1984; Bennett, 1996). However, in coastal waters the main source of tributyltin is antifouling coatings on vessel hulls.

The International Maritime Organisation placed a restriction on the use of tributyltin as an active agent in antifouling coatings on the hulls of vessels <25 m in the late 1980's, due to its toxicity to nontarget organisms. The International Convention on the Control of Harmful Antifouling Systems on Ships adopted in 2001 prohibited the use of tributyltin as an antifouling agent on new coatings applied to vessels by 2003 and its presence on all vessels unless sealed with approved sealer coats by 2008. In South Africa, the use of tributyltin on vessels <25 m has been banned, but no regulations are in place for larger vessels.

and/or tributyltin were Mono-, diat concentration above the method detection limit in sediment at each station where analysed (Figure 16; data in Appendix 5). By far the highest tributyltin concentration was found in sediment at Station DD near the Prince Edward Graving Dock in Congella Basin (Figure 16). The concentration at other stations in Congella Basin was considerably higher than elsewhere in the port apart from Station Y near the T-Jetty. There is little doubt the high tributyltin concentrations in sediment in Basin reflect activities Congella at vessel construction and maintenance operations considering the historical use of tributyltin in vessel antifouling coatings. There is a strong probability the high concentrations reflect the inclusion of tributyltin-impregnated antifouling coatings in the sediment.

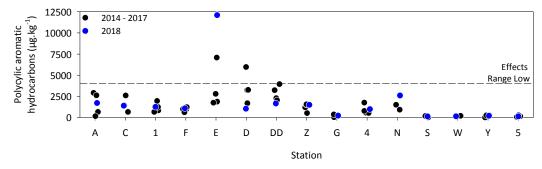
The high tributyltin concentration found in sediment at Station Y near the T-Jetty is interesting since it is far higher than concentrations measured at this station in previous surveys (see further below). For example, the concentration measured in sediment at this station in surveys made in 2015, 2016 and 2017 was 1.2, <0.5 and 160 μg.kg<sup>-1</sup> respectively compared to 940 μg.kg<sup>-1</sup> in 2018. The reason is uncertain, but based on the nature of the sediment (low mud fraction) it is assumed this variability reflects the inclusion of tributyltin-impregnated antifouling coating flakes in the sediment.

# 3.6. Historical trends for organic chemicals and tributyltin

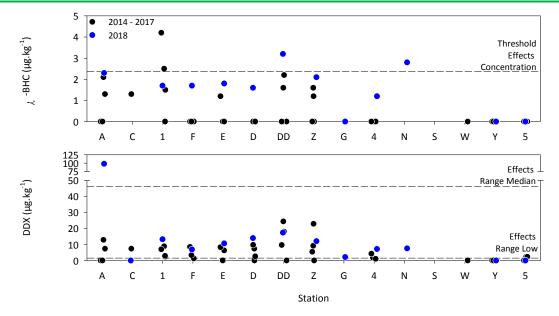
As is the case for metals there is value in examining long-term trends for organic chemical and tributyltin concentrations in sediment between surveys. Since organic chemicals are analysed in sediment at far fewer station than metals, only periodically at certain of these stations, and at few stations in the lower part of the Bay the comparison is less informative regarding spatial trends in contamination.

Polycyclic aromatic hydrocarbon concentrations have always been found in sediment when analysed, but typically at considerably higher concentrations in the upper part of the Bay (Figure 19). However, the concentrations have varied widely amongst stations, and at some stations in the upper part. The highest, or amongst the highest concentrations were more or less consistently found at Stations D, DD and E in Congella Basin. Concentrations at Stations 1, F and Z, also in Congella Basin, have usually been somewhat lower. This difference in concentration amongst stations separated by a short distance in Congella Basin was discussed above and alludes to significant local sources of these chemicals or hydrodynamic factors that facilitate their local accumulation in sediment.

Lindane concentrations have shown no clear temporal or spatial trend apart from only being found in sediment in the upper part of Durban Bay (Figure 20). DDT and its degradation products DDD and DDE have been common contaminants of sediment in the upper part of, but far less common in the lower part. In fact, they have only been



**Figure 19.** Total polycyclic aromatic hydrocarbon concentrations in sediment collected in Durban Bay between 2014 and 2018. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station 5 in the Point Basin (see Figure 2).



**Figure 20.** Lindane and DDX concentrations in sediment collected in Durban Bay between 2014 and 2018. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station 5 in the Point Basin (see Figure 2). Organochlorine pesticides were never analysed in sediment at Station S, but a position for this station is included in the graph to be consistent with the graph for polycyclic aromatic hydrocarbons.

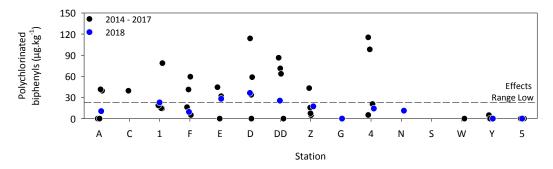
found in sediment Station 5 in two of the five surveys when analysed, and then at a very low (and identical) concentration, but never at Stations W and Y.

Polychlorinated biphenyls have been widespread contaminants of sediment in the upper part of Durban Bay, although their concentration has varied widely between surveys at any station where they have been analysed more than once (Figure 21). Concentrations in sediment in the upper part were typically considerably higher than in the lower part, where they have in fact not been found at two of the three stations where analysed. At Station Y these chemicals have been recorded in one of the five surveys when analysed, but at a very low concentration.

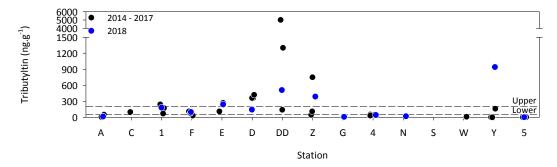
Tributyltin has also been a widespread contaminant

of sediment in Durban Bay, although the concentration has varied widely between surveys at any station, and amongst stations (Figure 21). Tributyltin concentrations in the upper part have typically been considerably higher than in the lower part. The highest concentrations were almost invariably in sediment at one or more of the stations in Congella Basin. This makes sense considering the wide use of tributyltin in antifouling coatings. However, as discussed above the concentration in sediment at Station Y near the T-Jetty in 2018 was by someway the highest measured at this station since 2014.

The findings show that there are sources of polycyclic aromatic hydrocarbons, pesticides and polychlorinated biphenyls in and to the port. The Amanzimnyama, Umbilo and Umhlatuzana Rivers appear to be important sources of these chemicals.



**Figure 21.** Total polychlorinated biphenyl concentrations in sediment collected in Durban Bay between 2014 and 2018. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station 5 in the Point Basin (see Figure 2). Polychlorinated biphenyls were never analysed in sediment at Station S, but a position for this station is included in the graph to be consistent with the graph for polycyclic aromatic hydrocarbons.



**Figure 22.** Tributyltin concentrations in sediment collected in Durban Bay between 2014 and 2018. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station 5 in the Point Basin (see Figure 2). Tributyltin was never analysed in sediment at Station S, but a position for this station is included in the graph to be consistent with the graph for polycyclic aromatic hydrocarbons.

Vessel maintenance and construction operations appear to be an important source of polycyclic aromatic hydrocarbons, but possibly also polychlorinated biphenyls. Lindane, DDX and polychlorinated biphenyl concentrations have often been elevated at Station 4 at Berths 2/3 in Maydon Wharf Channel, suggesting there is localised source of these chemicals in this area. This could be stormwater runoff entering through an outfall at this site, or through the Canal Road culvert.

As stated above there is little doubt that the largest sources of butyltins are vessel construction and maintenance operations and its leaching from antifouling coatings, although there is a possibility that there could be sources to the port as the uses of tributyltin is not restricted to antifouling coatings.

# 3.7. Comparison of chemical concentrations to sediment quality guidelines

The ultimate concern when sediment is found to be contaminated is whether the contaminants are at

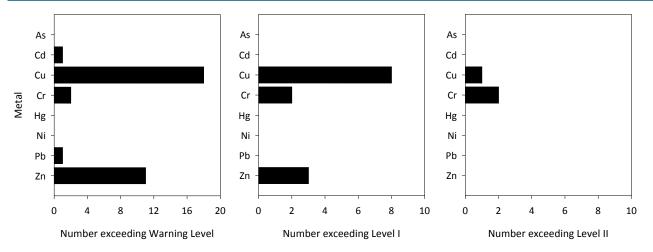
concentrations that are high enough to adversely affect biological receptors through toxicity, and in the context of dredging and dredged material disposal if the contaminants may pose a toxic risk to receptors at the dredging and dredged material disposal sites. As stated above, the National Environmental Management Act: Integrated Coastal Management Act, 2008 (Act No. 24 of 2008) governs the openwater disposal of dredged material, but not the act of dredging itself. The permitting process is thus concerned with potential impacts associated with the act of disposing dredged material at sea. The potential impacts of dredged material disposal are numerous. One impact that can be assessed through the analysis of contaminant concentrations in sediment is the transfer of contaminants in the sediment to a dredged material disposal site. The contaminants can impact on sediment-dwelling organisms at the disposal site directly through acute toxicity or chronic toxicity, and may indirectly affect organisms over a wider scale by contaminant uptake and transfer through the food web. Other concerns of dredged material disposal relate to the physical disturbance of organisms at the disposal site through burial by dredged material, scouring as the dredged material sediment is transported off the disposal site by currents, and changes in sediment granulometry that affect organisms that have a requirement for sediment of a specific grain size, and increased turbidity which may have numerous impacts on organisms. However, these

are not considered in in the permitting process in South Africa (and often not in other parts of the world).

The most effective approaches to determining if contaminants in sediment are adversely affecting sediment-dwelling organisms through toxicity is to test the toxicity of sediment in the laboratory,

**Table 2.** Sediment quality guidelines used to estimate the toxicological significance of chemical concentrations in sediment collected in Durban Bay in June 2018. Metal concentrations as  $\mu g.g^{-1}$  dry weight, other chemicals as  $\mu g.kg^{-1}$  dry weight. ERL = Effects Range Low, ERM = Effects Range Median, TEC = Threshold Effects Concentrations, PEC = Probable Effects Concentration.

	Enviror	ment of imental airs	_	; et al. 995)		PAR 11)		ald <i>et al.</i> 900)
Chemical	Level I	Level II	ERL	ERM	Lower	Upper	TEC	PEC
Metals								
Arsenic	57	93						
Cadmium	5.1	9.6						
Chromium	260	370						
Copper	230	390						
Lead	218	530						
Mercury	0.84	1.5						
Nickel	140	370						
Zinc	410	960						
Pesticides								
p,p'-DDE			2.2	27				
DDT			1.58	46.1				
γ-BHC (gamma, Lindane)							2.37	4.99
Dieldrin							1.9	61.8
Polychlorinated biphenyls								
Total PCBs			22.7	180				
Polycyclic aromatic hydrocarbons								
Naphthalene			160	2100				
Acenaphthylene			44	640				
Acenaphthene			16	500				
Fluorene			19	540				
Phenanthrene			240	1500				
Anthracene			85.3	1100				
Sum low molecular weight			552	3160				
Fluoranthene			600	5100				
Pyrene			665	2600				
Benzo(a)anthracene			261	1600				
Chrysene			384	2800				
Benzo(a)pyrene			430	1600				
Dibenzo(ah)anthracene			63.4	260				
Sum high molecular weight			1700	9600				
PAH (sum)			4022	44792				
Butyltin								
Tributyltin					50	200		

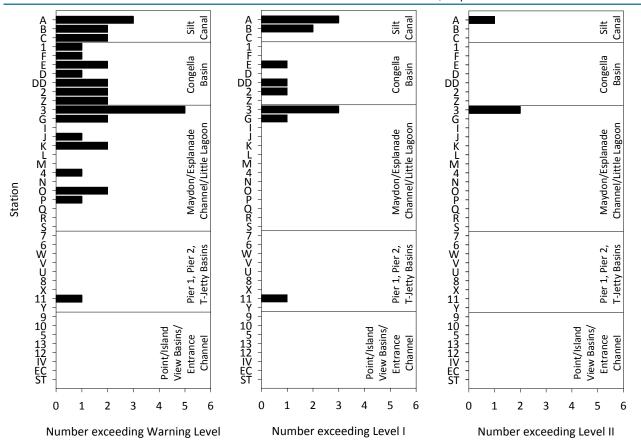


**Figure 23.** The number of stations at which metals in sediment collected in Durban Bay in June 2018 were at a concentration that exceeded the Warning Level, Level I and Level II of the sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal.

and/or to assess the health of communities of invertebrate organisms that live in and on sediment. These approaches are time consuming and expensive and in ports are not always definitive because numerous other disturbances, such as dredging and vessel propeller wash, may result in changes to these communities that resemble changes induced by the toxic effects contaminants. In South Africa, there are in any case no whole sediment toxicity testing procedures. When whole sediment toxicity testing and/or the analysis of benthic invertebrate communities is not possible most investigators estimate the risk posed by contaminants in sediment by comparing their concentrations to sediment quality guidelines. This is in spite of the well-documented limitations of sediment quality guidelines, perhaps the most important being that they assume the entire concentration of chemicals in sediment is in a bioavailable form. The comparison of chemical concentrations to sediment quality guidelines forms one tier of dredging decision-making frameworks used in many countries. If chemical concentrations exceed sediment quality guidelines this triggers the requirements of subsequent tiers in the framework, which often require further testing (e.g. toxicity testing) to determine if the contaminants are toxic to pelagic and benthic organisms.

A dredging decision-making framework for South Africa has not been formulated. The Department of Environmental Affairs has defined sediment quality guidelines that it uses to decide if sediment identified for dredging in South African ports is suitable for openwater disposal. However, there are only guidelines for metals. There are three guidelines, known as the Warning Level, Level I and Level II (Table 2). The Warning Level provides a warning of incipient metal contamination but is not used for decision-making. Sediment with metals at a concentration below the Level I is considered suitable for openwater disposal. Sediment with metals at a concentration between the Level I and Level II is considered cause for concern, with the degree of concern increasing as the concentrations approach the Level II. Further testing may be requested to determine if metals in the sediment pose a toxic risk to sediment-dwelling organisms, but in practice this has not been implemented. Sediment with metals at a concentration exceeding the Level II is considered unsuitable for openwater disposal unless other evidence (e.g. toxicity testing) shows the metals are not toxic to sedimentdwelling organisms due, for example, to the metals being present in metal flecks or metal-impregnated paint flakes and the entire concentration thus not being in a bioavailable form.

The number of metal concentrations in sediment collected in Durban Bay in June 2018 that exceed the South African sediment quality guidelines is provided in Figures 23 and 24. The copper concentration in sediment at 18 stations, zinc concentration in sediment at 11 stations, chromium concentration in sediment at two stations, and

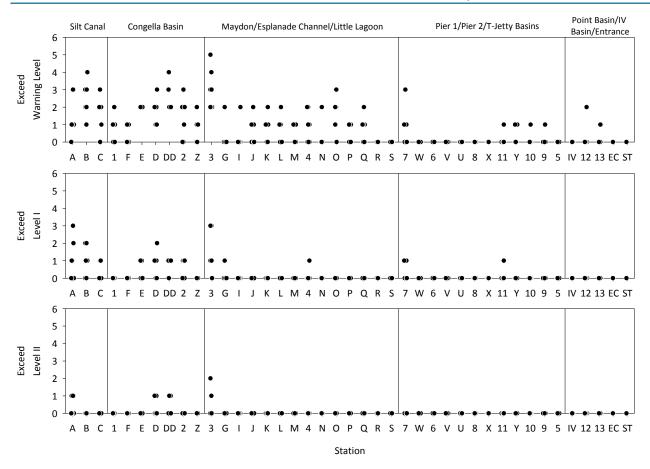


**Figure 24.** The number of metals in sediment collected in Durban Bay in June 2018 that were at a concentration exceeding the Warning Level, Level I and Level II of the sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station ST at the eastern most part of the south breakwater in the entrance channel (see Figure 2).

cadmium and lead concentration in sediment at single stations exceed the Warning Level. The copper, zinc and chromium concentration in sediment at eight, three and two of the stations also exceed Level I, and the copper and chromium concentration at Station 3 and concentration at Station A the Level II. The copper concentration in sediment at Stations A and 2 and the zinc concentration in sediment at Station 3 is only slightly lower than the Level II. The greatest risks associated with the disposal of sediment in Durban Bay are thus for sediment in Congella Basin and nearby parts of Maydon Wharf Channel. Although sediment in the Silt Canal is also contaminated this part of the Bay is very rarely dredged.

The concentrations of several metals in sediment in the upper part of Durban Bay have often exceeded the Warning Level in surveys since 2014, but far less often in the lower part (Figure 24). Fewer concentrations have exceeded the Level I, largely restricted to sediment in the upper part of the Bay. Metal concentrations exceeding the Level II were restricted to Station A off the inflow of the Umbilo/Umhlatuzana Rivers, Stations D and DD in Congella Basin, and Station 3 at Berth 9/10 in Maydon Wharf Channel.

As stated above, the South African sediment quality guidelines only provide guidelines for metals. Consequently, sediment quality guidelines derived for coastal waters in North America by Long et al. and for freshwater ecosystems MacDonald et al. (2000) were used to estimate the toxicological significance of the organic chemicals analysed for which there is a guideline (Table 2). Long et al. (1995) derived two guidelines, namely the Effects Range Low and Effects Range Median. The **Effects** Range Low represents concentration below which a chemical is unlikely to be toxic to sediment-dwelling organisms, while the Effects Range Median represents the concentration above which toxic effects are likely. Concentrations between the guidelines pose a potential risk, with the potential increasing as the concentration



**Figure 25.** The number of metals in sediment collected in Durban Bay between 2014 and 2018 that were at a concentration exceeding the Warning Level, Level I and Level II of the sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal. The stations are arranged in sequence from Station A in the Silt Canal in the upper part of the Bay to Station ST at the eastern most part of the south breakwater in the entrance channel (see Figure 2).

approaches the Effects Range Median. The Long *et al.* (2000) sediment quality guidelines do not provide guidelines for Lindane and Dieldrin. It was for this reason that the sediment quality guidelines derived by MacDonald *et al.* (2000) were used. MacDonald *et al.* (2000) derived two guidelines, namely the Threshold Effect Concentration and Probable Effect Concentration. The guidelines have the same narrative intent as sediment quality guidelines derived by Long *et al.* (1995).

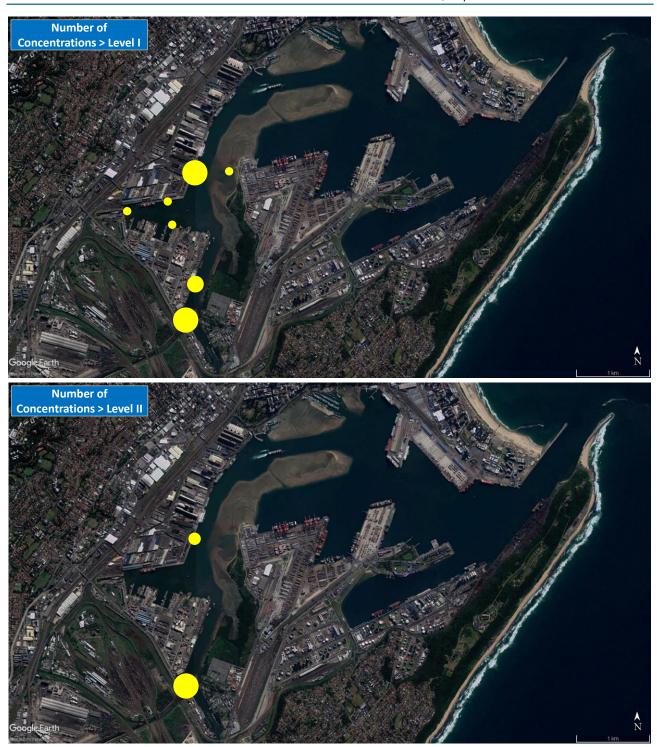
The total polycyclic aromatic hydrocarbon concentration in sediment collected at Station E at the Ship Repair Jetty in Congella Basin far exceeds the Effects Range Low, but is well below the Effects Range Median (Figure 13). The concentrations at other stations were generally well below the Effects Range Low.

The Lindane concentration at two stations slightly exceeds the Threshold Effect Concentration, but is below the Probable Effects Concentration (Figure

14). The Dieldrin concentration at two stations also slightly exceeds the Threshold Effect Concentration, but is well below the Probable Effects Concentration (Figure 14). The DDX concentration in sediment at the ten stations where it was detected exceeds the Effects Range Low, but is well below the Effects Range Median apart from Station A in the Silt Canal (Figure 14). The concentration at Station A far exceeds the Effects Range Median.

The total polychlorinated biphenyl concentration in sediment at four stations slightly exceeds the Effects Range Low, but is well below the Effects Range Median (Figure 15).

The Long *et al.* (1995) and MacDonald *et al.* (2000) sediment quality guidelines do not provide guidelines for tributyltin. A perusal of the literature shows that sediment quality guidelines for tributyltin vary widely from one jurisdiction to another. In Europe, for example, the lower guideline varies from  $3-100~\mu g.kg^{-1}$  and the upper

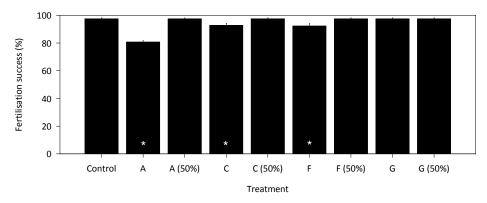


**Figure 26.** Bubble plot illustrating the number of metal concentrations in sediment collected in Durban Bay in June 2018 that exceed the Level I (top) and Level II (bottom) of the sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal. The bubbles are scaled to show differences between stations. The largest bubble for Level I represents three metals and for the Level II represents two metals.

guideline from 7 - 1000  $\mu g.kg^{-1}$ . Scientists from the Coastal Systems research group of the CSIR defined sediment quality criteria for tributyltin based on OSPAR (2011) guidelines for assessing the status of tributyltin contamination of sediment based on the incidence of imposex in gastropods (Table 2). The tributyltin concentration in sediment at seven of

the ten stations where analysed exceeds the lower guideline. The concentration at four of the stations also exceeds the upper guideline, considerably so in the case of Stations DD, Z and Y (Figure 16).

The total polycyclic aromatic hydrocarbon concentration in three sediment samples collected



**Figure 27.** Fertilisation success (mean ± standard deviation) of sea urchin (*Tripneustes gratilla*) gametes exposed to elutriates of sediment collected in Durban Bay in June 2018. Two treatments were tested, namely the raw elutriate and a 50% dilution. Asterisks denote the fertilisation success was statistically significantly lower than that for the control.

at two stations since 2014 has exceeded the Effects Range Low, but all were well below the Effects Range Median. The Lindane concentration in a few sediment samples slightly exceeded the Threshold Effects Concentration, but all were well below the Probable Effects Concentration. A large proportion of DDX concentrations have exceeded the Effects Range Low, but only one has also exceeded the Effects Range Median. A large proportion of total polychlorinated biphenyl concentrations have exceeded the Effects Range Low, but none has exceeded the Effects Range Median. The tributyltin concentration in numerous sediment samples has exceeded the Lower guideline, and a fairly high number of concentrations in sediment in Congella Basin have also exceeded the Upper guideline.

#### 3.8. Toxicity testing

The fertilisation success of sea urchin gametes exposed to raw and 50% dilutions of elutriates prepared using sediment collected at four stations in Durban Bay in June 2018 are provided in Figure 20. The fertilisation success for gametes exposed to raw elutriates for Stations A and C in the Silt Canal and Station F in Congella Basin was statistically significantly lower than that for the control. In other words, the raw elutriates were toxic to sea urchin gametes. There was no toxicity evident when the elutriates were diluted by 50% with clean seawater. Raw and 50% diluted elutriates for Station G presented no toxicity to sea urchin gametes.

The elutriate test is designed to simulate water quality for up to about four hours after the openwater disposal of dredged sediment, or after contaminant release at a dredging site (either directly from sediment or in hopper overflow water if a trailer-suction hopper dredger is used). The implication of the elutriate toxicity testing is that the dredging of sediment at stations in Durban Bay for which testing was performed, and openwater disposal of dredged sediment could lead to the remobilisation/release of contaminants into the water column at concentrations that may pose an acute toxic risk to pelagic organisms. However, it is uncertain if this will only be restricted to organisms or their life stages that are similarly sensitive to toxicants as sea urchin gametes. One challenge with toxicity testing using sea urchin gametes is that they are highly sensitive toxicants, including ammonia and hydrogen sulphide that are commonly found at high concentrations in sediment porewater. However, these chemicals/ compounds usually do not pose a risk to most marine animals in a dredging context as they are usually rapidly oxidised to less toxic forms after their release from sediment. It is not known how much ammonia or hydrogen sulphide was present in the sediment tested for toxicity in 2018.

### 4. Conclusions

Sediment at numerous stations in Durban Bay was metal contaminated in June 2018. The sediment at most stations in the Silt Canal, Congella Basin and Maydon Wharf and Esplanade Channels was enriched by at least one metal, although the number decreased markedly along Maydon Wharf and Esplanade Channels. The most significantly metal contaminated was in the Silt Canal and Congella Basin, and part of Maydon Wharf Channel.

Copper was the most frequently enriched metal in sediment, followed by chromium and zinc. These have been the, or amongst the most frequently enriched metals in sediment in Durban Bay in previous surveys. The Amanzimnyama and Umbilo/ Umhlatuzana Rivers appear to be important vectors for the introduction of anthropogenic metals to the Silt Canal, while vessel maintenance and construction operations appear to be the most important anthropogenic source of metals to Congella Basin.

The trend in metal contamination of sediment in Durban Bay in June 2018 is consistent with the findings of previous surveys. The same metals were often repeatedly enriched in sediment at certain stations between surveys, although the magnitude of enrichment has varied and the suite of metals enriched was not always identical. This probably reflects differences in the grain size composition of sediment at stations between surveys, small-scale and temporal variability in the presence of metal flecks, metal-impregnated antifouling coating flakes and metal ore particles in the sediment, and the removal of contaminated sediment by dredging amongst other factors. The highest, or amongst the highest cadmium, cobalt, copper, chromium, nickel and zinc concentrations measured in sediment in Durban Bay since 2011 were for sediment collected in 2018, although this was usually restricted to one or two stations and from an overall perspective the magnitude and extent of metal contamination was comparable to previous surveys.

The sediment at most stations in the upper part of Durban Bay where these chemicals were analysed in June 2018 was contaminated by polycyclic aromatic hydrocarbons, organochlorine pesticides, tributyltin and polychlorinated biphenyls, but less frequently in the lower part by organochlorine pesticides and polychlorinated biphenyls. In fact, organochlorine pesticides and polychlorinated biphenyls were only contaminants of sediment in the upper part, although the sediment collected at few stations in the lower part was analysed. Although butyltins were present in sediment at all stations, concentrations in the upper part of the Bay were generally considerably higher than in the lower part. The notable exception was Station Y the T-Jetty, where the tributyltin near

concentration was far higher than in previous surveys.

The difference in the contamination of sediment between the upper and lower parts of Durban Bay undoubtedly reflects a complex interplay of factors, including the hydrodynamic regime, nature of sediment, and proximity to anthropogenic sources contaminants. Vessel maintenance construction operations in Congella Basin are an of important source polycyclic aromatic hydrocarbons and tributyltin, and possibly also polychlorinated biphenyls. However, there is little doubt there are other sources of these chemicals to Durban Bay. The source of the pesticides is less certain, but probably reflects inputs via rivers and surface runoff.

The toxicological risk posed by metals and organic chemicals in sediment was estimated using sediment quality guidelines. Metal concentrations were compared to the sediment quality guidelines used by the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is suitable for openwater disposal. The copper, zinc and chromium concentration in sediment at eight, three and two stations exceeds the Level I, and the copper and chromium concentration at one and chromium concentration at another station also exceed the Level II.

The toxicological risk posed by organic chemicals in sediment in Durban Bay was estimated by comparing their concentrations to sediment quality guidelines used in North American coastal waters by Long et al. (1995) and MacDonald et al. (2000), or to guidelines derived by OSPAR (2011). The total polycyclic aromatic hydrocarbon concentration in sediment at one station exceeds the Effects Range Low but is well below the Effects Range Median. The concentration of Lindane and Dieldrin at some stations slightly exceed the Threshold Effect Concentration. The DDX concentration in sediment at ten stations where it was detected exceeds the Effects Range Low, and at one station also the Effects Range Median. The total polychlorinated biphenyl concentration in sediment at four stations slightly exceeds the Effects Range Low, but is well below the Effects Range Median. The tributyltin concentration in sediment at seven stations exceeds the Lower guideline, while that at four stations also exceeds the Upper guideline.

Exceedance of sediment quality guidelines by concentrations of numerous chemicals in sediment in Durban Bay in June 2018 suggests they may be posing a toxic risk to sediment-dwelling organisms.

Elutriates prepared using sediment collected at three of four stations in the upper part of Durban Bay was toxic to sea urchin gametes, but not when diluted by 50% using clean seawater. The elutriate test is designed to simulate water quality about four hours after the openwater disposal of dredged sediment, or after contaminant release at a dredging site (either directly from sediment or in hopper overflow water if a trailer-suction hopper dredger is used). The implication of the elutriate toxicity testing is that the dredging of sediment at stations in Durban Bay for which testing was performed, and openwater disposal of dredged sediment could lead to the remobilisation/release of contaminants into the water column at concentrations that may pose an acute toxic risk to pelagic organisms. However, it is uncertain if this will only be restricted to organisms or their life stages that are similarly sensitive to toxicants as sea urchin gametes.

Based on the comparison of metal and organic chemical concentrations in sediment collected in Durban Bay in June 2018 to sediment quality guidelines the greatest risk due to contaminant remobilisation during dredging will be in the Silt Canal, Congella Basin and part of Maydon Wharf Channel. There is also a potential risk of contaminant release when sediment dredged from these areas is disposed at the dredged material disposal site offshore of Durban. Contaminants in the sediment will be translocated to the dredged material disposal site, but it seems unlikely finegrained contaminated sediment will remain for long on the seabed due to the highly dispersive nature of this environment.

#### 5. References

Alzieu C, Sanjuan J, Deltreil JP and Borel M (1986)
Tin contamination in Arcachon Bay: effects on oyster shell anomalies. *Marine Pollution Bulletin* 17: 494-498.

- Anderson L (2004) Imposex in the City: A Survey to Monitor the Effects of TBT Contamination in Port Curtis, Queensland. Cooperative Research Centre for Coastal Zone Estuary and Waterway Management, Technical Report 16.
- ATSDR (Agency for Toxic Substances and Disease Registry) (2000) Toxicological Profile for *Polychlorinated Biphenyls*. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Online at: http://www.atsdr.cdc.gov/toxprofiles/tp17.html.
- Baars AJ, Bakker MI, Baumann RA, Boon PE, Freijer JI, Hoogenboom LAP, Hoogerbrugge R, van Klaveren JD, Liem AKD, Traag WA and de Vries J (2004) Dioxins, dioxin-like PCBs and non-dioxin-like PCBs in foodstuffs: occurrence and dietary intake in The Netherlands. *Toxicology Letters* 151: 51-61.
- Batelle (2007) Final sediment trap study report for field monitoring to evaluate the utility of sediment traps and polyethelene samplers to characterize dissolved and particulate PCB concentrations in New Bedford Harbor.

  Submitted to the United States Environmental Protection Agency, Narragansett Laboratory.
- Batterman SA, Chernyak SM, Gounden Y, Matooane M and Naidoo RN (2008) Organochlorine pesticides in ambient air in Durban, South Africa. *Science of the Total Environment* 397: 119-130.
- Baumard P, Budzinski H, Guarrigues P, Dizer H and Hansen PD (1999) Polycyclic aromatic hydrocarbons in recent sediments and mussels (*Mytilus edulis*) from the Western Baltic Sea: occurrence, bioavailability and seasonal variations. *Marine and Environmental Research* 47: 17-47.
- Bellas J, Albentosa M, Vidal-Liñán L, Besada V, Franco MA, Fumega J, González-Quijano A, Viñas L and Beiras R (2014) Combined use of chemical, biochemical and physiological variables in mussels for the assessment of marine pollution along the N-NW Spanish coast. *Marine Environmental Research* 96: 105-117.
- Bergen BJ, Nelson WG, Mackay J, Dickerson D, Jayaraman S. 2005. Environmental monitoring of remedial dredging at the New Bedford Harbor, MA, Superfund site. *Environmental*

- Monitoring and Assessment 111: 257-275.
- Boehm PD (2006) Polycyclic aromatic hydrocarbons (PAHs). In: Morrison RD and Murphy BL (Eds), *Environmental Forensics. Contaminant Specific Guide.* Elsevier: New York, NY.
- Blocksom KA Walters DM, Jicha TM, Lazorchak JM, Angradi TR and Bolgrien DW (2010) Persistent organic pollutants in fish tissue in the midcontinental great rivers of the United States. Science of the Total Environment 408: 1180-1189.
- Caetano M, Madureira M-J and Vale C (2002) Metal remobilisation during resuspension of anoxic contaminated sediment: short-term laboratory study. *Water, Air and Soil Pollution* 143: 23-40.
- Diamanti-Kandarakis E, Bourguignon J-P, Giudice LC, Hauser R, Prins GS, Soto AM, Zoeller RT and Gore AC (2009) Endocrine-disrupting chemicals: an Endocrine Society scientific statement. *Endocrine Reviews* 30: 293-342.
- Di Toro DM, Mahony JD, Hansen DJ, Scott KJ, Hicks MB, Mays SM and Redmond MS (1990) Toxicity of cadmium in sediments: The role of acid-volatile sulfide. *Environmental Toxicology and Chemistry* 9: 1487-1502.
- Douben PET (Ed) (2003) *PAHs: An Ecotoxicological Perspective*. John Wiley and Sons, Chichester, UK.
- Eggleton J and Thomas KV (2004) A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. *Environmental International* 30: 973-980.
- Förstner U (1989) Contaminated sediments. In: Bhattacharji S, Friedman GM, Neugebauer HJ, Seilacher A (Eds), *Lecture notes in earth sciences*. Springer Verlag, Berlin.
- Goosens H and Zwolsman JJG (1996) An evaluation of the behaviour of pollutants during dredging activities. *Terra et Aqua* 62: 20-27.
- Hanson P, Evans D, Colby D and Zdanowics V (1993)

  Assessment of elemental contamination in estuarine and coastal environments based on geochemical and statistical modeling of sediments. *Marine Environmental Research* 36: 237-266.
- Hites RA, LaFlamme RE and Windsor JG (1980)
  Polycyclic aromatic hydrocarbons in the marine/aquatic sediments: Their ubiquity. In:
  Petrakis L and Weiss FT (Eds), *Petroleum in the*

- *Marine Environment*. American Chemical Society, Washington, DC.
- IARC (International Agency for Research on Cancer) (1991) Occupational exposures in insecticide application, and some pesticides. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. IARC, Lyon, France.
- Karickhoff S, Broen D and Scott T (1979) Sorption of hydrophobic pollutants on natural sediments. *Water Research* 18: 241-248.
- Keith L and Telliard W (1979) Priority pollutants, I A perspective view. *Environmental Science and Technology* 13: 416-423.
- Kersten M and Smedes F (2002) Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. *Journal of Environmental Monitoring* 4: 109-115.
- Lima AL, Farrington JW and Reddy CM (2005) Combustion-derived polycyclic aromatic hydrocarbons in the environment - a review. *Environmental Forensics* 6: 109-131.
- Long E, MacDonald D, Smith S and Calder F (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19: 81-97.
- Loring DH and Rantala RTT (1992) Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Review* 32: 235-283.
- Luch A (2005) *The carcinogenic effects of polycyclic aromatic hydrocarbons.* London: Imperial College Press.
- MacDonald DD, Ingersoll CG and Berger TA (2000)

  Development and evaluation of consensusbased sediment quality guidelines for
  freshwater ecosystems. Archives of
  Environmental Contamination and Toxicology
  39: 20-31.
- Mahler BJ, Van Metre PC, Bashara TJ, Wilson JT and Johns DA (2005) Parking lot sealcoat: An unrecognized source of urban polycyclic aromatic hydrocarbons. *Environmental Science and Technology* 39: 5560-5566.
- McCready S, Slee DJ, Birch GF and Taylor SE (2000)
  The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. *Marine Pollution Bulletin* 40: 999-1006.
- Means JC, Wood SG, Hassett JJ and Banward WL

- (1980) Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environmental Science and Technology* 14: 1524-1528.
- Mostert MMR, Ayoko GA and Kokot S (2010) Application of chemometrics to analysis of soil pollutants. *Trends in Analytical Chemistry* 29: 430-435.
- Neff JM (1979) Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Sources, Fates, and Biological Effects. Applied Science, London, Great Britain.
- Newman BK and Watling RJ (2007) Definition of baseline metal concentrations for assessing metal enrichment of sediment from the southeastern Cape coastline of South Africa. *Water SA* 33: 677-694.
- Noller BN (2003) Critical review of the environmental fate of TBT and its toxicological effects on the Pacific oyster Crassostrea gigas including at Georges Bay and other Tasmanian locations. National Research Centre for Environmental Toxicology.
- Oceanica Consulting (2005) Investigation into Tributyltin (TBT) Contamination in Cockburn Sound. Prepared for Department of the Environment by Oceanica Consulting Pty Ltd. Report No. 457/1.
- OSPAR Commission (2011) *Background document on organic tin compounds*. ISBN 978-1-907390-76-0. Publication Number: 535/2011.
- Qiu JW, Chan KM and Leung KMY (2011) Seasonal variations of imposex indices and butyltin concentrations in the rock shell *Thais clavigera* collected from Hong Kong waters. *Marine Pollution Bulletin* 63: 482-488.
- Rae JE and Allen JRL (1993) The significance of organic matter degradation in the interpretation of historical pollution trends in depth profiles of estuarine sediment. *Estuaries* 16: 678-682.
- Reitsema TJ and Spickett JT (1999) Imposex in Morula granulata as bioindicator of tributyltin (TBT) contamination in the Dampier Archipelago, Western Australia. *Marine Pollution Bulletin* 39: 280-284.
- Reitsema TJ, Field S and Spickett JT (2003) Surveying imposex in the coastal waters of

- Perth, Western Australia, to monitor trends in TBT contamination. *Australasian Journal of Ecotoxicology* 9: 87-92.
- Rice DC and Hayward SH (1997) Effects of postnatal exposure to a PCBs mixture in monkeys on nonspatial discrimination reversal and delayed alternation performance. *Neurotoxicology* 18: 479-494.
- Schropp SJ, Lewis FG, Windom HL, Ryan JD, Calder FD and Burney LC (1990) Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. *Estuaries* 13: 227-235.
- Stahl LL, Snyder BD, Olsen AR and Pitt JL (2009) Contaminants in fish tissue from US lakes and reservoirs: a national probabilistic study. *Environmental Monitoring and Assessment* 150: 3-19.
- Stillman JE, Meyers PA and Eadie BJ (1998)
  Perylene: An indicator of alteration processes
  or precursor materials? *Organic Geochemistry*29: 1737-1744.
- Stronkhorst J and Van Hattum B (2003) Contaminants of concern in Dutch marine harbor sediments. *Archives of Environmental Contamination and Toxicology* 45: 306-316.
- Taylor SR and McLennan SM (1981) The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. *Philosophical Transactions of the Royal Society, London* 301: 381-399.
- USEPA (United States Environmental Protection Agency) (2009) Far field water quality monitoring (resuspension). Available at: http://www.hudsondredgingdata.com/Monitoring/Water.
- USEPA (United States Environmental Protection Agency) (2011) 2010 biennial national listing of fish advisories. EPA-820-F-11-014.
- Wedepohl KH (1995) The composition of the continental crust. *Geochimica et Cosmochimimica Acta* 59: 1217-1232.
- Xue W and Warshawsky D (2005) Metabolic activation of polycyclic and heterocyclic aromatic hydrocarbons and DNA damage: a review. *Toxicology and Applied Pharmacology* 206: 73-93.

### 6. Appendices

Appendix 1

Global Positioning System coordinates of stations sampled in Durban Bay in June 2018.

Station	Latitude	Longitude
Α	29°53'53.64"S	31°00'14.61"E
В	29°53'38.62"S	31°00'19.20"E
С	29°53'22.50"S	31°00'25.94"E
1	29°53'16.08"S	31°00'29.87"E
F	29°53'13.39"S	31°00'14.44"E
E	29°53'12.34"S	31°00'07.71"E
D	29°53'11.37"S	30°59'59.37"E
DD	29°53'06.45"S	30°59'45.16"E
2	29°53'02.83"S	31°00'05.56"E
Z	29°53'06.10"S	31°00'20.80"E
3	29°52'49.78"S	31°00'19.95"E
G	29°52'56.42"S	31°00'34.57"E
I	29°52'45.98"S	31°00'26.62"E
J	29°52'40.79"S	31°00'28.90"E
K	29°52'34.72"S	31°00'31.44"E
L	29°52'29.07"S	31°00'35.21"E
M	29°52'23.62"S	31°00'39.12"E
4	29°52'10.71"S	31°00'43.26"E
N	29°52'08.08"S	31°00'54.70"E
0	29°52'07.94"S	31°01'02.10"E
Р	29°52'06.61"S	31°01'12.53"E
Q	29°52'04.65"S	31°01'22.85"E
R	29°52'02.28"S	31°01'34.60"E
S	29°51'49.56"S	31°01'14.14"E
7	29°51'57.90"S	31°02'00.14"E
6	29°52'43.10"S	31°01'05.19"E
W	29°52'33.59"S	31°01'11.12"E
V	29°52'51.22"S	31°01'24.96"E
U	29°52'58.28"S	31°01'28.67"E
8	29°52'48.85"S	31°01'40.73"E
X	29°52'29.65"S	31°01'38.41"E
11	29°52'35.37"S	31°01'47.77"E
Y	29°52'24.08"S	31°01'55.64"E
9	29°52'46.88"S	31°01'57.14"E
10	29°52'11.24"S	31°02'08.35"E
5	29°52'40.75"S	31°02'31.27"E
13	29°52'42.40"S	31°03'05.41"E
12	29°53'04.56"S	31°02'33.74"E
IV	29°53'15.72"S	31°01'52.61"E
ec	29°52'15.18"S	31°03'22.21"E
st	29°51'53.57"S	31°03'50.57"E

Copy of South African National Accreditation System (SANAS) certificate for the environmental chemistry laboratory at the CSIR campus in Stellenbosch.



## CERTIFICATE OF ACCREDITATION

In terms of section 22(2) (b) of the Accreditation for Conformity Assessment, Calibration and Good Laboratory Practice Act, 2006 (Act 19 of 2006), read with sections 23(1), (2) and (3) of the said Act, I hereby certify that:-

# COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH ANALYTICAL LABORATORY

### STELLENBOSCH

Facility Accreditation Number: T0093

is a South African National Accreditation System accredited Testing laboratory provided that all SANAS conditions and requirements are complied with

This certificate is valid as per the scope as stated in the accompanying schedule of accreditation Annexure "A", bearing the above accreditation number for

### CHEMICAL ANALYSIS

The facility is accredited in accordance with the recognised International Standard

### ISO/IEC 17025:2005

The accreditation demonstrates technical competency for a defined scope and the operation of a laboratory quality management system

While this certificate remains valid, the Accredited Facility named above is authorised to use the relevant SANAS accreditation symbol to issue facility reports and/or certificates

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Mr R Josias Chief Executive Officer

Effective Date: 01 August 2013 Certificate Expires: 31 July 2018 C S I R JAN CILLIER STR.

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Contribution (%) of grain size class fractions and total organic content to the bulk weight and mean grain size (mm) of sediment collected in Durban Bay in June 2018. VCS = very coarse-grained sand, CS = coarse-grained sand, MS = medium-grained sand, FS = fine-grained sand, VFS = very fine-grained sand, TOC = total organic content.

Station	Gravel	VCS	CS	MS	FS	VFS	Mud	Mean	TOC
Α	0.00	0.00	0.08	1.12	9.13	8.97	80.70	0.07	11.49
В	0.00	0.00	0.28	0.62	2.22	0.55	96.33	0.04	7.53
С	0.26	0.11	0.18	1.31	18.67	10.72	68.76	0.06	2.70
1	0.00	0.00	0.33	2.36	15.95	11.40	69.97	0.06	2.67
F	0.37	0.73	2.74	17.86	26.28	4.61	47.41	0.12	1.85
E	0.49	0.18	0.45	2.14	11.70	4.60	80.45	0.06	2.60
D	0.00	0.11	0.57	6.33	21.59	6.41	64.99	0.07	1.92
DD	0.10	0.10	0.50	5.68	27.20	4.19	62.23	0.08	2.71
2	0.00	0.00	0.17	0.43	2.40	1.11	95.88	0.04	3.07
Z	0.05	0.15	1.32	8.90	20.94	4.45	64.19	0.08	2.80
3	0.07	0.31	1.45	15.88	28.33	3.60	50.36	0.09	2.02
1	0.02	0.32	2.89	52.72	32.54	1.93	9.57	0.24	0.61
J	0.11	0.19	0.53	2.62	33.64	7.34	55.57	0.07	2.62
K	0.00	0.00	0.23	1.24	14.25	6.67	77.60	0.06	2.50
L	0.00	0.08	0.52	19.59	62.03	5.62	12.15	0.20	0.53
М	0.00	0.18	1.19	21.35	39.94	5.26	32.08	0.13	1.59
4	0.00	0.12	0.79	10.29	26.84	3.65	58.31	0.08	2.25
N	0.03	0.14	2.24	25.20	38.60	4.99	28.80	0.14	2.36
0	0.00	0.00	0.23	0.53	7.07	3.42	88.75	0.05	4.44
Р	0.00	0.00	0.21	2.91	22.68	4.02	70.18	0.07	3.87
Q	0.00	0.23	2.06	22.77	49.12	4.97	20.85	0.14	1.13
R	0.05	0.18	0.32	3.00	33.63	14.87	47.94	0.09	1.99
S	0.19	0.19	0.68	31.00	61.97	3.95	2.02	0.21	0.72
7	0.09	0.13	0.30	5.54	38.85	5.85	49.24	0.09	1.69
6	0.05	0.20	3.78	45.59	39.20	2.27	8.91	0.23	0.29
W	0.00	0.05	0.32	34.94	44.83	3.12	16.74	0.16	0.91
V	0.09	0.20	1.36	31.89	44.25	4.88	17.32	0.16	0.42
U	0.00	0.00	0.52	35.24	44.11	4.91	15.22	0.19	0.65
8	0.72	1.79	5.12	31.02	31.43	3.52	26.40	0.15	0.73
Х	0.07	0.37	2.06	38.06	40.43	3.08	15.92	0.17	0.28
11	2.58	1.13	1.32	39.32	41.93	3.09	10.63	0.22	0.54
Υ	1.03	0.32	1.42	55.71	35.27	1.83	4.42	0.25	0.20
9	0.06	0.39	1.81	28.82	29.11	3.36	36.46	0.13	1.76
10	0.10	0.88	2.86	41.69	29.66	3.41	21.41	0.16	0.62
5	0.00	0.05	1.38	54.54	28.95	3.92	11.16	0.24	0.51
13	0.17	1.76	8.56	47.89	28.93	4.44	8.26	0.25	0.55
12	0.25	0.90	4.35	43.57	38.25	3.20	9.48	0.23	0.53
IV	0.08	0.45	3.78	52.32	35.15	1.60	6.62	0.25	0.30
ec	0.02	0.46	6.10	44.58	28.06	10.12	10.66	0.25	0.63
st	0.00	0.08	3.37	59.10	35.51	0.87	1.06	0.26	0.24

Metal concentrations (Al and Fe as mg.g<sup>-1</sup>, other metals as μg.g<sup>-1</sup> dry weight) in sediment collected in Durban Bay in June 2018. Al - aluminium, Fe - iron, As - arsenic, Ba = barium, Be = beryllium, Cd = cadmium, Co = cobalt, Cu = copper, Cr = chromium, Mn = manganese, Hg = mercury, Ni = nickel, Pb = lead, V = vanadium, Zn = zinc, < = concentration below the method detection limit as indicated. Bold text in coloured cells indicates the concentration exceeds the Warning Level, Level I and Level II of the sediment quality guidelines used by Branch Oceans and Coasts of the Department of Environmental Affairs to decide if sediment identified for dredging in South African ports is of a suitable quality for openwater disposal.

Station	Al	Fe	As	Ва	Be	Cd	Со	Cu	Cr	Mn	Hg	Ni	Pb	٧	Zn
Α	41.08	36.98	3.11	205.46	1.27	0.88	34.93	360.17	539.84	566.66	0.20	79.80	93.00	66.91	644.24
В	43.48	44.02	10.93	211.85	1.31	0.80	21.37	299.50	243.40	342.15	0.21	41.44	94.90	84.56	554.95
С	29.98	28.16	5.67	136.16	0.81	0.43	14.27	180.50	164.35	188.15	0.20	23.85	70.40	56.72	277.42
1	31.65	30.96	7.72	142.06	0.96	0.54	12.35	162.11	139.43	234.54	0.19	20.88	64.30	59.65	261.11
F	30.28	26.59	9.60	106.58	0.65	0.28	12.97	166.50	131.84	217.15	0.13	19.57	62.20	46.46	258.28
E	40.08	39.92	10.65	205.76	1.09	0.40	17.97	268.50	200.69	288.15	0.24	28.62	88.10	77.26	367.90
D	28.08	28.90	7.54	131.81	0.79	0.21	11.37	218.50	153.52	191.15	0.14	20.78	47.30	59.60	216.52
DD	36.18	32.68	8.48	137.60	0.96	0.25	13.03	301.17	163.71	295.66	0.24	20.88	78.00	63.25	308.42
2	48.80	48.87	13.97	214.27	1.30	0.45	17.60	327.11	230.92	531.04	0.29	30.07	91.00	93.88	405.10
Z	31.00	29.02	7.59	118.30	0.84	0.32	12.60	170.27	249.00	256.83	0.27	22.23	75.40	56.55	273.02
3	34.50	34.37	7.23	186.77	0.79	1.40	25.84	542.53	568.17	391.52	0.07	48.31	161.00	86.04	951.95
G	41.40	40.26	14.63	172.51	1.02	0.42	16.50	264.11	211.79	568.04	0.25	27.50	104.00	78.74	376.39
I	7.67	5.48	4.10	20.71	0.19	0.06	2.92	26.36	19.00	59.32	0.03	3.84	12.60	12.05	41.39
J	28.30	26.82	10.38	112.23	0.67	0.28	12.33	148.56	122.53	252.37	0.16	18.67	58.20	57.42	231.35
K	36.70	36.27	16.06	154.86	0.84	0.33	15.33	192.56	157.60	424.37	0.22	24.30	72.00	73.95	313.13
L	12.00	8.24	5.24	32.89	0.23	0.07	4.04	31.76	32.90	128.37	0.04	5.17	17.20	18.44	57.26
M	17.70	16.01	10.16	66.03	0.37	0.13	7.20	73.76	55.02	173.37	0.10	10.97	30.60	34.71	122.60
4	29.20	28.29	8.87	116.83	0.76	0.28	10.80	132.11	97.04	291.04	0.18	20.38	52.20	55.86	216.31
N	16.00	14.75	5.53	66.99	0.37	0.20	7.19	89.56	61.33	127.37	0.12	10.47	51.00	32.10	176.54
0	44.10	41.63	18.28	167.04	0.90	0.30	15.93	178.56	147.40	590.37	0.26	24.44	71.30	83.09	301.82
Р	31.60	32.49	15.07	134.85	0.72	0.21	12.73	130.56	112.97	469.37	0.20	19.45	52.90	67.86	221.78
Q	12.15	11.01	5.15	45.74	0.32	0.08	3.95	38.32	45.89	174.33	0.07	6.94	20.80	23.88	69.40
R	20.70	20.94	8.35	80.54	0.61	0.14	7.49	71.87	96.00	244.83	0.17	12.54	37.80	40.46	139.91
S	3.18	2.26	0.27	13.03	0.10	0.07	0.78	8.87	16.57	29.33	0.02	2.29	9.01	6.04	26.73
7	26.80	24.19	10.04	108.13	0.58	0.15	8.88	85.51	75.37	274.04	0.25	15.32	42.80	48.12	161.50
6	8.69	6.33	1.71	23.65	0.20	0.05	2.93	14.11	16.21	122.04	0.02	4.52	6.20	12.97	30.30
W	11.69	10.54	2.72	35.37	0.31	0.07	4.32	26.88	26.52	109.69	0.05	5.91	11.30	21.00	49.21
V	10.80	8.57	2.93	37.04	0.31	0.10	2.39	23.47	39.90	140.83	0.04	5.12	17.50	17.92	45.61

Station	Al	Fe	As	Ba	Be	Cd	Со	Cu	Cr	Mn	Hg	Ni	Pb	V	Zn
U	8.90	6.92	2.61	33.13	0.25	0.08	2.31	18.77	41.18	99.83	0.03	4.13	10.20	15.40	37.95
8	16.00	12.75	3.87	42.70	0.33	0.07	4.13	19.61	38.71	153.04	0.03	6.54	9.42	24.98	38.65
X	12.00	10.02	5.13	37.83	0.33	0.04	2.86	14.17	28.68	119.83	0.04	5.43	9.80	20.18	30.64
11	11.13	8.19	4.33	43.02	0.25	0.08	3.57	251.00	28.06	149.15	0.04	4.30	9.32	17.79	86.02
Υ	8.91	8.18	3.32	37.32	0.23	0.04	3.36	18.30	38.89	91.35	0.02	3.73	8.81	18.01	27.03
9	18.20	17.47	7.83	71.15	0.42	0.12	7.18	79.81	95.77	293.04	0.13	10.83	25.10	34.20	111.04
10	14.50	14.95	6.58	63.06	0.29	0.07	5.03	30.01	51.71	186.04	0.13	6.65	31.10	22.89	73.72
5	6.71	5.51	1.21	18.71	0.18	0.04	2.71	10.68	15.40	56.49	0.03	3.44	4.18	12.52	21.02
13	7.80	7.01	4.37	33.84	0.23	0.03	3.80	29.80	34.30	204.15	0.04	3.60	8.38	15.31	26.33
12	8.91	8.18	3.32	37.32	0.23	0.04	3.36	18.30	38.89	91.35	0.02	3.73	8.81	18.01	27.03
IV	6.40	5.02	3.21	19.99	0.16	0.08	1.61	11.77	23.01	69.63	0.02	3.14	6.56	11.22	21.85
ec	9.87	8.49	4.05	37.22	0.22	0.05	3.86	15.23	23.26	113.52	0.02	4.98	5.30	19.66	23.52
st	5.25	5.22	5.24	20.86	0.16	0.03	1.66	2.30	12.49	85.73	< 0.01	2.39	2.18	11.48	8.54
Warning Level	-	-	42	-	-	1.2	-	110	250	-	0.43	88	110	-	270
Level I	-	-	57	-	-	5.1	-	230	260	-	0.84	140	218	-	410
Level II	-	-	93	-	-	9.6	-	390	370	-	1.5	370	530	-	960

**Appendix 5** 

Polycyclic aromatic hydrocarbon, organochlorine pesticide, polychlorinated biphenyl, and butyltin concentrations (μg.kg<sup>-1</sup> dry weight) in sediment collected in Durban Bay in June 2018. < = concentration below the method detection limit as indicated.

Chemical	Α	С	1	F	E	D	DD	Z	G	4	N	S	W	Υ	5
Polycyclic aromatic hydrocarbons															
Naphthalene	50	21	23	47	240	15	25	35	7	26	31	<5	<5	<5	<5
2-Methylnaphthalene	55	18	26	59	220	14	49	47	8	23	25	<5	20	<5	12
Acenaphthylene	32	17	12	<25	65	10	25	<25	<4	9	25	<4	<4	<4	<4
Acenaphthene	25	11	13	<25	577	10	25	<25	<4	8	25	<4	<4	<4	<4
Fluorene	25	14	16	<25	437	9	29	<25	<4	16	37	<4	<4	<4	<4
Phenanthrene	115	87	77	107	1310	55	98	94	17	95	253	12	10	12	12
Anthracene	28	26	21	<25	74	18	25	27	<4	17	56	<4	<4	<4	<4
Fluoranthene	185	145	117	122	1950	93	172	136	21	98	360	20	7	16	9
Pyrene	182	134	102	118	1440	89	163	141	21	92	294	18	8	17	9
Benz(a)anthracene	162	102	67	64	687	62	105	92	13	57	199	11	<4	13	<5
Chrysene	122	110	70	78	932	71	114	98	17	66	190	12	8	13	9
Benzo(b+j)fluoranthene	137	142	110	96	967	106	167	142	22	92	261	13	10	22	9
Benzo(k)fluoranthene	36	47	43	45	436	34	53	67	8	37	91	7	<4	8	<4
Benzo(e)pyrene	94	101	77	74	596	73	116	105	17	66	179	10	8	15	7
Benzo(a)pyrene	105	99	74	66	616	74	113	98	14	61	179	11	<5	16	<5
Perylene	40	110	238	81	273	150	95	166	16	66	79	<4	9	9	<5
Benzo(g,h,i)perylene	125	91	74	75	545	70	134	111	19	68	181	10	9	17	7
Dibenz(a,h)anthracene	26	27	19	<25	144	20	28	26	4	18	44	<4	<4	4	<4
Indeno(1,2,3-c,d)pyrene	109	66	54	48	453	51	85	74	12	46	123	7	<5	12	<4
Coronene	57	26	24	<25	108	20	37	29	6	22	44	<5	<5	5	<5

Chemical	Α	1	F	E	D	DD	Z	G	4	N	Υ	5
Organochlorine pesticides												
НСВ	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptachlor epoxide	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Aldrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
γ-BHC (Lindane)	2	1.7	1.7	1.8	1.6	3	2.1	<1	1.2	2.8	<1	<1
α-BHC	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
β-ВНС	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

Chemical	Α	1	F	Е	D	DD	Z	G	4	N	Υ	5
Organochlorine pesticides												
δ-ΒΗС	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
trans-Chlordane	1	<1	<1	<1	<1	<1	<1	<1	<1	1.1	<1	<1
cis-Chlordane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Oxychlordane	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	3	<1	<1	1.2	<1	2	<1	<1	<1	1.2	<1	<1
p'p'-DDE	5	4.6	3.3	5.4	4.4	7	6	<1	2.6	3.4	<1	<1
p'p'-DDD	6	3.3	2.4	2.3	2.2	4	3.7	2.2	2.3	2.6	<1	<1
p'p'-DDT	87	5.4	1.2	3	7.4	6	2.4	<1	2.3	1.6	<1	<1
Endrin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin Aldehyde	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endrin Ketone	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
α-Endosulfan	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
β-Endosulfan	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Endosulfan Sulfate	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Methoxychlor	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

Chemical	Α	1	F	E	D	DD	Z	G	4	N	Υ	5
Polychlorinated biphenyls												
PCB # 8	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 18	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 28	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 44	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 52	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 66	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 77	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 101	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 105	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 118	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 126	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 128	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 138	3	3.6	2.1	4.7	5.8	6	4	<2	3.3	2.6	<2	<2
PCB # 153	2	4.3	2.2	5.1	5.2	6	3.9	<2	3.2	2.5	<2	<2
PCB # 169	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 170	<2	<2	<2	<2	2.1	<2	<2	<2	<2	<2	<2	<2

Chemical	Α	1	F	E	D	DD	Z	G	4	N	Υ	5
Polychlorinated biphenyls												
PCB # 180	<2	2.5	<2	3	3.5	<2	<2	<2	<2	<2	<2	<2
PCB # 187	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 195	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 206	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
PCB # 209	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2

Chemical	Α	1	F	Е	D	DD	Z	G	4	N	Υ	5
Butyltins												
Monobutyltin as Sn	<0.5	1.7	1.3	<0.5	0.68	2	1	12	2.5	1.4	96	2
Dibutyltin as Sn	24	170	110	230	140	520	324	17	50	37	370	3
Tributyltin as Sn	15	180	98	240	143	510	387	7.4	43	20	940	2

Fertilisation success (%) of sea urchin (*Tripneustes gratilla*) gametes after exposure to raw and 50% dilutions of elutriates prepared using sediment collected in Durban Bay in June 2018.

Treatment	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Control	97	98	98	97
Α	82	80	81	80
A (50%)	98	98	97	97
F	94	92	93	90
F (50%)	98	98	97	97
С	92	91	94	94
C (50%)	98	98	97	97
G	98	98	97	97
G (50%)	98	98	97	97